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NBSIR 74-373

# LIQUEFIED NATURAL GAS RESEARCH

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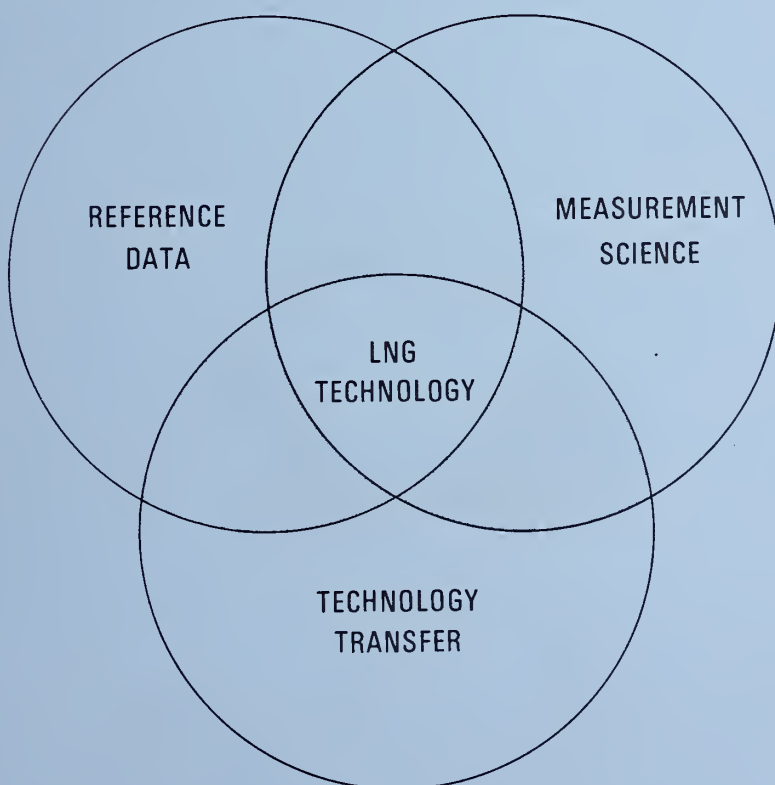
*at the*

# NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD

1 JAN - 30 JUNE, 1974

D. B. Mann, Editor



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1974



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# LIQUEFIED NATURAL GAS RESEARCH *at the* NATIONAL BUREAU OF STANDARDS

D. B. Mann, Editor

Cryogenics Division  
Institute for Basic Standards  
National Bureau of Standards  
Boulder, Colorado 80302

Progress Report for the Period  
1 Jan - 30 June, 1974



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U.S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

Prepared for:

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LNG Density Project Steering Committee  
(in cooperation with the American Gas Association)

Pipeline Research Committee  
(American Gas Association)

Federal Power Commission  
Bureau of Natural Gas  
Washington, DC 20426

General Services Administration  
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U. S. Department of Commerce  
National Bureau of Standards  
Office of Standard Reference Data  
Washington, DC 20234

Aerospace Safety Research and Data Institute  
National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135



## ABSTRACT

Seventeen cost centers supported by seven other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at a 20 man-year level with funding expenditures of over \$500,000. This integrated progress report to be issued in January and July is designed to:

- 1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.
- 2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.
- 3) Provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paper work at the cost center level.

The contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature.

Key words: Cryogenic; liquefied natural gas; measurement; methane; properties; research.

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1. Title. Refractive Index of Fluid Methane  
Principle Investigator. James D. Olson
2. Cost Center Number. 2750122
3. Sponsor Project Identification. NBS-NRC Postdoctoral Research Associate Program.
4. Introduction. This experimental program will provide accurate measurements of the refractive index of liquid and gaseous methane. The data can be related to the fluid density by the Lorenz-Lorentz electromagnetic equation of state and, as such, offers the possibility of fluid density gauging by optical techniques. This pure fluid data is essential to the possible study of mixture refractive index properties.
5. Objectives or Goals. The refractive index of liquid and vapor methane will be measured along the two-phase saturation boundary. In addition, gaseous isotherms will be obtained at 220 K, 250 K, 280 K, and 300 K at pressures to 200 atm. Low pressure isotherms will be measured below the saturation boundary.
6. Background. The high precision interferometric technique used to measure the refractive index was developed in this laboratory by D. E. Diller (J. Chem. Phys. 49, 3096 (1968)). An improved optical data gathering method was the principal modification of this technique. Prior to this reporting period, a literature survey of Lorenz-Lorentz and Clausius-Mossotti virial equation data was conducted. A cryostat was constructed using the design of Diller. The temperature measurement problems described in the previous report were eliminated after modification of the apparatus in December and January.
7. Program and Results. All of the essential measurements of the refractive index of fluid methane were completed during this reporting period. These data include the saturated liquid and vapor and the gas isotherms above the critical point. Table 1 lists the saturation data. The measurements were made at the Hg<sup>198</sup> green line,  $\lambda = 546.22705$  nm.

The refractive index data were combined with the experimental densities of Goodwin and Prydz<sup>1</sup> to calculate the Lorenz-Lorentz function,

$$LL = \frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho}.$$

Figure 1 is a preliminary sketch of the trends exhibited by the LL function.  $A_r$  is the zero density limit of the LL function at 300 K. The saturated vapor LL data may be about 0.3%-0.5% too small because uncertainties in the vapor densities. The saturated liquid LL function decreases sharply at higher densities in contrast to the Clausius-Mossotti function previously obtained by Straty and Goodwin<sup>2</sup>. The LL data for all the gas isotherms are represented within 0.05% by the fitted equation,  $LL = 6.6081 + (0.00679)\rho - (0.0003439)\rho^2$ .

The critical refractive index,  $n_c$ , was obtained by use of the rectilinear diameter law on the saturated liquid and vapor refractive index data ( $T_c = 190.555$  K). The critical refractive index was combined with an estimate of the critical LL function, indicated by the diamond on Figure 1, to calculate an estimate of critical density;  $\rho_c = 10.15 \pm 0.01$  mole/l. The critical density uncertainty was calculated from the error bounds on  $LL_c$  in Figure 1. This is a preliminary value and differs from that currently used. Further analysis will be necessary to determine the best value for the critical density.

8. Problem Areas. There are no problems at this time.

9. Funding. January 1 - June 30, 1974

|             |        |                |
|-------------|--------|----------------|
| Labor       | 0.5 MY | 17.0 K\$       |
| Other Costs |        | <u>4.0 K\$</u> |
| Total       |        | 21.0 K\$       |
| Remaining   |        | 8.5 K\$        |

10. Future Plans. The data will be reduced and a manuscript prepared during the next two months. Some additional experimental data will be taken as well. This is an NRC-Postdoctoral Appointment which terminates near the end of September 1974 and thus, this effort will be completed prior to that time.

| Schedule               | July | Aug. | Sept. |
|------------------------|------|------|-------|
| Further Experiments    |      | →    |       |
| Data Analysis          |      | →    |       |
| Manuscript Preparation |      |      | →     |

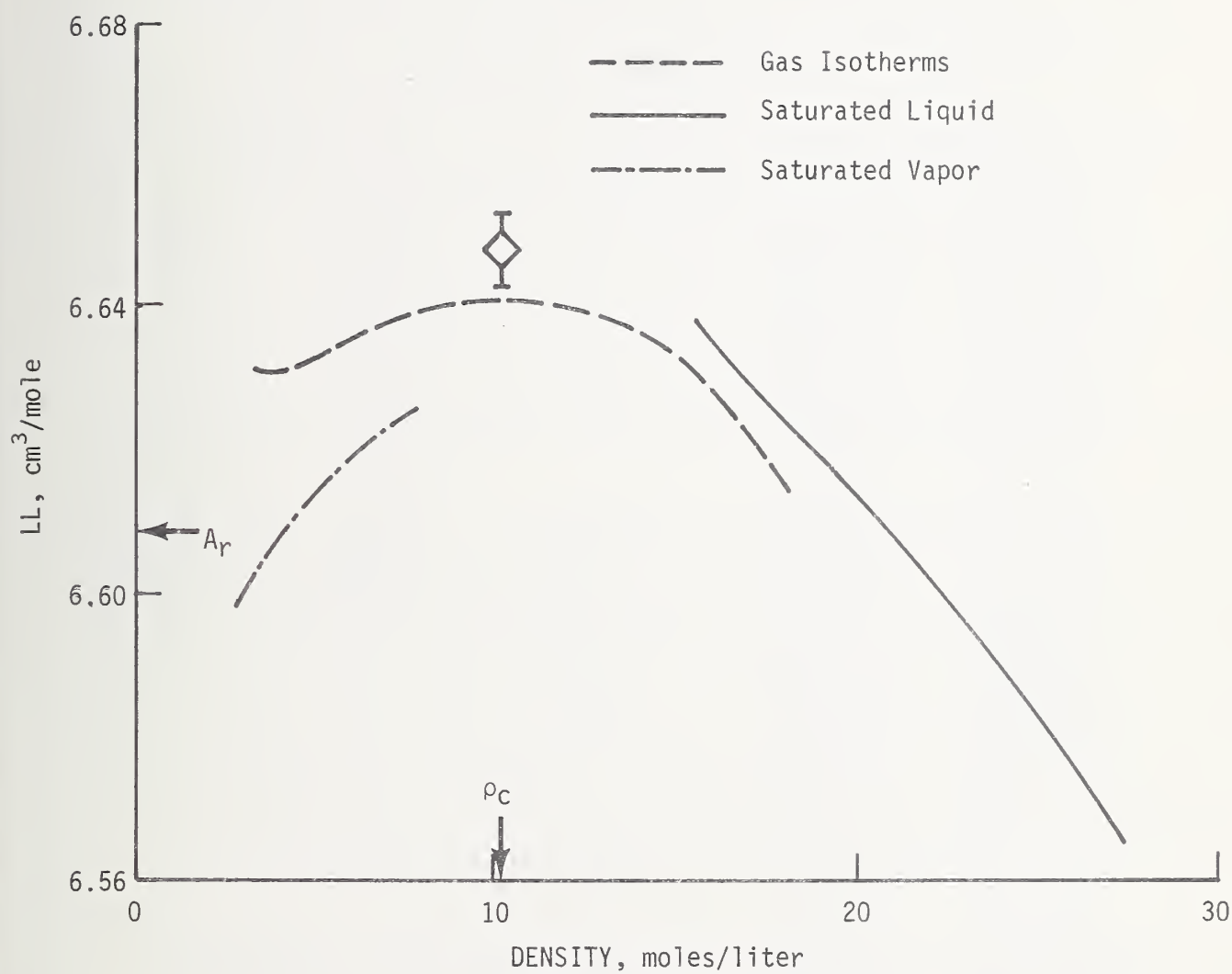


FIGURE 1. LL Function vs. Density

# References.

1. R. D. Goodwin and R. Prydz, J. Res. NBS 76A, 81 (1972).
2. G. C. Straty and R. D. Goodwin, Cryogenics 13, 712 (1973).

Table 1. Refractive Index of Methane at Saturation

| Saturated Liquid |                        | Saturated Vapor |                        |
|------------------|------------------------|-----------------|------------------------|
| T(K)             | n                      | T(K)            | n                      |
| 95.000           | 1.291925               | 99.290          | 1.00041                |
| 100.000          | 1.287281               | 114.403         | 1.00139                |
| 105.000          | 1.282518               | 129.865         | 1.00374                |
| 110.000          | 1.277639               | 139.649         | 1.00622                |
| 115.000          | 1.272646               | 150.000         | 1.01016                |
| 120.000          | 1.267505               | 160.000         | 1.015746               |
| 125.000          | 1.262206               | 172.386         | 1.026976               |
| 130.000          | 1.256717               | 176.928         | 1.033134               |
| 135.000          | 1.251031               | 180.000         | 1.038404               |
| 140.000          | 1.245083               | 182.000         | 1.042540               |
| 145.000          | 1.238853               | 186.000         | 1.053738               |
| 150.000          | 1.232279               | 190.000         | 1.078959               |
| 155.000          | 1.225270               |                 |                        |
| 160.000          | 1.217739               |                 |                        |
| 165.000          | 1.209538               |                 |                        |
| 170.000          | 1.200455               |                 |                        |
| 175.000          | 1.190055               |                 |                        |
| 178.000          | 1.182914               |                 |                        |
| 180.000          | 1.177615               |                 |                        |
| 181.000          | 1.174749               |                 |                        |
| 182.000          | 1.171708               |                 |                        |
| 183.000          | 1.168460               |                 |                        |
| 184.000          | 1.164957               |                 |                        |
| 185.000          | 1.161138               |                 |                        |
| 186.000          | 1.156889               |                 |                        |
| 187.000          | 1.152056               |                 |                        |
| 188.000          | 1.146359               |                 |                        |
| 189.000          | 1.139107               |                 |                        |
| 189.404          | 1.135383               |                 |                        |
| 190.555          | 1.10326 <sub>7</sub> * | 190.555         | 1.10326 <sub>7</sub> * |

\* extrapolated  $n_c$



1. Title. Fluid Transport Properties  
Principal Investigator. Howard J. M. Hanley
2. Cost Center Number. 2750124
3. Sponsor Project Identification. NBS-Office of Standard Reference Data
4. Introduction. Studies of mixtures have not received the attention or support that have been given to equivalent studies of pure fluids. This is especially true for transport properties where the mixture effort has been negligible. Yet from the standpoint of the liquefied natural gas industry mixtures are more important than pure fluids. At this time there is no adequate method in existence for predicting the transport properties of fluid mixtures even in the dilute regions. Properties cannot be measured for all possible mixtures, thus adequate predictions methods are needed in order to supply the necessary design data needed to increase efficiency and reduce costs.
5. Objectives or Goals. The long range or continuing goal of the program is to perform a systematic study of the theories and experimental measurements relating to transport properties, specifically the viscosity and thermal conductivity coefficients, of simple mixtures over a wide range of experimental conditions. The specific objectives of the program include: 1) the systematic correlation of the transport properties of simple binary mixtures and the development of prediction techniques, 2) development of a mixture theory for the dilute gas region and the dense gas and liquid regions, 3) extension of the theory and prediction techniques to multicomponent systems, and 4) suggested guidelines for future areas of experimental work.
6. Background. A program was started in 1965 with the goal of producing tables of fluid transport properties through many approaches; e.g., data correlation and evaluation, statistical mechanics, kinetic theory, thermodynamics and statistics. A theory was developed based on a modification of the Enskog theory. In addition, a systematic study of new potential function, the M-6-8. The theoretical studies along with data analysis results in prediction techniques for the dilute gas region for monatomic and polyatomic fluids. These techniques were then successfully extended to the dense gas and liquid regions. To date tables of transport properties have been prepared for argon, krypton, xenon, oxygen, nitrogen, fluorine and hydrogen. In addition an analytical representation of the anomalous behavior of the thermal conductivity coefficient in the "critical region"

has been developed. As a precursor to the study of fluid mixtures we have started a task to apply numerical techniques such as molecular dynamics to transport properties. To this end the Principal Investigator is in Australia gaining experience in advanced theoretical techniques. During the current reporting period a molecular dynamics model has been modified and applied to methane. The program has been run for a system of 108 methane molecules. The resulting output are, in effect, experimental data and will be compared with methane data and equations of state from the Cryogenics Division.

8. Problem Areas. There are no problem areas at this time.

9. Funding. January 1 - June 30, 1974

|             |               |                |
|-------------|---------------|----------------|
| Allocation  | 53.5 K\$      | OSRD           |
| Labor       | 0.5 MY        | 20.3 K\$       |
| Other Costs |               | <u>0.4 K\$</u> |
|             | Total         | 20.7 K\$       |
|             | Funding FY 75 | 53.5 K\$       |

10. Future Plans. The mixture part of the program will begin after August 1974. If the methane calculations prove successful, it may be possible to make preliminary calculations on binary systems of methane with ethane and nitrogen during the next year.

1. Title. LNG Fuels Safety  
Principal Investigators. Neil A. Olien and A. F. Schmidt
2. Cost Center Number. 2750427
3. Sponsor Project Identification. National Aeronautics and Space Administration, Cleveland, Ohio, Aerospace Safety Research and Data Institute. Order No. C-39327-C.
4. Introduction. The NASA-Aerospace Safety Research and Data Institute (ASRDI) was established to provide a focal point for information and research in aerospace safety. One of the areas of concern for ASRDI is Cryogenic Fluid Safety. In fact, this was the first area of effort for ASRDI. The thrust of the program is two-fold: first, to provide an automated information bank for retrieving references, and second, to publish series of state-of-the-art reviews. The information system is now operational and contains over 5000 references in cryogenic fluid safety. In addition, ASRDI has published approximately ten reviews.

Until this time, ASRDI has focused its attention and efforts on the two primary cryogenic propellants, hydrogen and oxygen. The oxygen work was started at NBS-Boulder in 1970 and the hydrogen work in 1972. With the coming possibility of methane or LNG fueled aircraft and the close affinity of LNG safety and cryogenic safety, ASRDI felt that it was timely to begin work in that area.
5. Objectives or Goals. The following objectives are to be achieved:
  - a) Review and modify an existing Cryogenic Fluids Safety Grid and thesaurus to include and adequately cover LNG safety.
  - b) Make a thorough search of over eleven information sources for LNG information. This will include published and unpublished material.
  - c) Catalog, index, abstract and put into machine readable form all available documents located in b) above. The indexing will be done by technical personnel with demonstrated competence in cryogenic safety and related fields.
6. Background. This program was started at NBS-Boulder by ASRDI in 1970. Since then considerable skill and experience has been gained in locating, processing and, most important, detailed subject indexing of safety-related information. In addition, NBS-Boulder has been

providing detailed coverage of the LNG field for the American Gas Association since early 1970. The present program, then, provides an opportunity for industry, government and the public to capitalize on the accumulated past efforts of two seemingly unrelated programs.

7. Program and Results. This NASA-funded program is not due to start until September 30, 1974, however, some preliminary work is being done on the thesaurus as well as some literature searching. We expect to locate some 400 safety-related papers which will be processed during the succeeding year. We also plan to publish, under a companion ASRDI Contract, a comprehensive thesaurus for Cryogenic Fluid Safety. This will include terminology pertinent to LNG safety.
8. Problem Areas. None
9. Funding. September 30, 1974 - October 1, 1975  
Allocation - FY 75 50 K\$ - NASA/ASRDI
10. Future Plans. We will begin processing safety-related documents in October and complete over 400 of them by October 1975. In addition, we will process carefully selected LNG/Methane/Methane Mixtures documents. Selection of these documents will be done in cooperation with other LNG projects within NBS.

1. Title. Properties of Cryogenic Fluids: Hypersonic (GHz) Velocity and Thermal Diffusivity Measurements  
Principal Investigator. G. C. Straty
2. Cost Center Number. 2750141
3. Sponsor. NBS
4. Introduction. Laser light scattering spectroscopy techniques will be used to obtain accurate thermophysical properties data for compressed and liquefied pure methane. This work will complement related work on the thermodynamic properties of the pure components of LNG mixtures (2750364). This work will provide data for the development of LNG technology at NBS and throughout the fuel gas industry.
5. Objectives or Goals. The objectives of this project are to obtain accurate sound velocity and thermal diffusivity data for pure methane (90-300 K, 350 bars) by using laser light scattering spectroscopy techniques. Sound velocity data are useful for testing the consistency of volumetric, calorimetric and thermodynamic properties data, and are potentially useful for density gauging applications. Thermal diffusivity data are useful for calculating transport properties data for LNG mixtures, required for performing heat transfer calculations.
6. Background. When light is incident on a perfectly homogeneous fluid, the reradiated (scattered) light field sums to zero in all but the exact forward direction. For a "real" fluid however, fluctuations, arising through various mechanisms, destroy the perfect homogeneity and results in the scattering of light in other directions as well. For example, thermally activated density fluctuations (phonons), propagating with the characteristic velocity of sound, give rise to scattered light which is doppler shifted in frequency from the incident light frequency and whose spectrum contains information on the sound velocity and attenuation. Local non-propagating temperature fluctuations, which decay diffusively, give rise to scattered light in a narrow frequency band about the incident light frequency and whose spectrum contains information on the lifetime of the fluctuations (thermal diffusivity). Since the frequency shifts are generally very small, it was not until the advent of the lasers with their extremely well defined frequency, that practical experiments using these phenomena were possible.

The application of laser light scattering techniques to obtaining thermophysical properties data was initiated to complement and check other measurement methods and to solve measurement problems in



inherent in more conventional methods. For example, laser light scattering techniques permit measurements of sound velocities for fluids and under conditions for which sound absorption is too large to perform ultrasonic measurements; laser light scattering techniques permit measurements of thermal diffusivities under conditions for which convection interferes with measurements of thermal conduction. The feasibility of light scattering experiments to obtain data on binary diffusion coefficients has also recently been demonstrated.

We have assembled and performance tested apparatus for laser light scattering spectroscopy measurements on compressed and liquefied gases (76-300 K, 350 bars). The apparatus consists of a copper optical cell with fused quartz windows, cryostat for refrigeration with liquid nitrogen, an argon ion laser, pressure scanned Fabry-Perot interferometer, and photon counting equipment.

7. Program and Results. Preliminary data on the hypersound velocities in pure methane have been obtained at low densities ( $< 14$  mol/l) where the large sound absorption in methane prohibits ultrasonic measurements. Data have been obtained along several isotherms from 210 K to 300 K at densities down to 1 mol/l. Agreement with previously measured ultrasonic velocities in the regions of overlapping data is good. Agreement with values calculated directly from PVT data is satisfactory.
8. Problem Areas. No significant problems have been encountered. Progress on the light scattering experiment has been determined primarily by our assignment of priorities to other LNG related efforts. The program to measure the hypersound velocities in pure methane is, however, progressing satisfactorily and on schedule.
9. Funding.

|                                      |          |
|--------------------------------------|----------|
| Man-years expended (Jan. -June 1974) | 0.3      |
| Equipment and/or Services Purchased  | 1.4 K\$  |
| Total Reporting Period Cost          | 15.0 K\$ |
| Balance Remaining (June 30, 1974)    | 0.0 K\$  |

10. Future Plans.

| Schedule: | year                                                                                                         | 1974 |   |
|-----------|--------------------------------------------------------------------------------------------------------------|------|---|
|           | quarter                                                                                                      | 3    | 4 |
| Methane:  | Measure hypersonic (GHz)<br>velocities in methane                                                            |      |   |
|           | Assemble and test apparatus<br>for Rayleigh line-width<br>(thermal diffusivity) mea-<br>surements on methane |      |   |

1. Title. Properties of Cryogenic Fluid Mixtures: Equilibrium Properties Data, Compilation and Evaluation, Prediction Methods  
Principal Investigators. M. J. Hiza, A. J. Kidnay (part time), and R. C. Miller (part time).
2. Cost Center Numbers. 2750142; 2750145
3. Sponsors. NBS; NBS-OSRD
4. Introduction. This project provides new experimental measurements on equilibrium properties and compilations of evaluated equilibrium properties data which are suitable for direct technological use or for the evaluation of prediction and calculation methods. This project supports the development of LNG technology in the areas of separation, purification, liquefaction and custody transfer by defining relationships between the composition, temperature, pressure, and equilibrium state properties for mixtures related to LNG.
5. Objectives or Goals. The overall objective of this project is to provide critically evaluated data, original and from other sources, on the phase equilibria and thermodynamic properties of cryogenic fluid mixtures. The program has been divided into the following elements:
  - a) Preparation of a comprehensive bibliography on experimental measurements of equilibrium properties for mixtures of selected molecular species of principal interest in cryogenic technology.
  - b) Selection and/or development of methods for correlation, evaluation and prediction of equilibrium properties data.
  - c) Retrieval and evaluation of experimental data for specific mixture systems selected on the basis of theoretical and/or technological importance.
  - d) Preparation of guidelines for future research based on the deficiencies noted in (a), (b), and (c).
  - e) Performing experimental research to alleviate deficiencies and provide a basis for improvement of prediction methods.
6. Background. A physical equilibria of mixtures research project was established in the Cryogenics Division in 1959. The initial effort, based on a bibliographic search and other considerations, was directed toward the acquisition of new experimental data on the solid-vapor and liquid-vapor equilibria and physical adsorption properties for a limited number of binary and ternary mixtures of components with widely



separated critical temperatures. Most of the systems studied included one of the light hydrocarbon species -- methane, ethane, or ethylene (ethene) -- with one of the quantum gases -- helium, hydrogen, or neon. The data for these systems led to significant improvements in the predictions of physical adsorption equilibrium and a correlation for the prediction of deviations from the geometric mean rule for combining characteristic energy parameters. In addition, significant new information was obtained for interaction third virial coefficients which was used in a correlation by one of our consultants, J. M. Prausnitz. The approach taken in this work has been as fundamental as possible with the intention of having an impact on a broad range of mixture problems.

Recent efforts have been directed toward problems associated with systems containing components with overlapping liquid temperature ranges, such as the nitrogen + methane system.

Preceding this reporting period, an expanded bibliography was prepared to update NBS Technical Note 56, published in May 1960 (objective a). Experimental liquid-vapor equilibria measurements were also completed at selected temperatures on the argon + methane systems.

7. Program and Results. The recent progress of this program is summarized as follows:

- a) A comprehensive bibliography of experimental data for ten equilibrium properties has been completed, reviewed, and revised. The final manuscript has been sent to a publisher selected by the OSRD. The bibliography includes sections on solid-liquid, solid-vapor, solid-liquid vapor, liquid-liquid, liquid-vapor, and gas-gas equilibria, as well as sections on liquid mixture densities, Joule-Thomson coefficients, and calorimetric measurements. The materials considered are hydrogen, helium-3, helium-4, deuterium, neon, carbon monoxide, nitrogen, oxygen, hydrogen sulfide, fluorine, argon, carbon dioxide, krypton, xenon, and the saturated and unsaturated hydrocarbons through the C<sub>4</sub>'s.

Because of its importance, the section on liquid-vapor equilibria was published as a survey paper in *Cryogenics* 13, 575 (Oct. 1973). It is anticipated that the complete bibliography will be published and available by late summer of this year.

- b) Work is currently in progress on the retrieval and evaluation of equilibria data for the methane + ethane system. Data for both argon + methane systems have been retrieved and evaluated. To

maintain this phase of the program within reasonable bounds, the only properties under study are liquid-vapor equilibria, liquid mixture densities, and gas or vapor mixture densities. This effort also requires selection of the pure vapor pressure and saturation densities. The new vapor pressure measurements of Wagner (Cryogenics 13, 1973) for nitrogen and argon have been programmed and compared with other data sets. As expected, there are significant discrepancies between data sets for the pure fluids which must be resolved.

- c) Our most recent liquid-vapor equilibria measurements for the nitrogen + methane system between 95 and 120 K are now being extended above the critical point of nitrogen to approximately 180 K. Preparations for these experiments were started during the last week of this reporting period.

8. Problem Areas. The major problem that may affect progress on the evaluation of mixtures data is the lack of generally accepted, rigorous methods for critically evaluating phase equilibria data. Each binary system poses special problems of its own, and it may be necessary to tailor the techniques employed.

9. Funding.

|                                      |          |
|--------------------------------------|----------|
| Man-years expended (Jan. -June 1974) | 0.6      |
| Equipment and/or Services Purchased  | 3.0 K\$  |
| Total Reporting Period Cost          | 38.0 K\$ |
| Balance Remaining (June 30, 1974)    | 0.0 K\$  |

# 10. Future Plans.

| Schedule:                                                                                                        | year    | 1974 |   |
|------------------------------------------------------------------------------------------------------------------|---------|------|---|
|                                                                                                                  | quarter | 3    | 4 |
| Retrieve phase equilibrium data for methane-ethane mixtures                                                      |         | →    |   |
| Select pure component ethane data                                                                                |         | →    |   |
| Calculate excess Gibbs energies for methane-ethane mixtures                                                      |         |      | → |
| Compare calculated excess Gibbs energies for different sets of data                                              |         |      | → |
| Compare calculated excess volume $V^E$ for different sets of data                                                |         |      | → |
| Complete phase equilibria measurements for the nitrogen-methane system between 120-180 K                         |         | →    |   |
| Analysis of nitrogen-methane data, comparisons, preparation of paper                                             |         |      |   |
| Prepare for new L-V equilibrium measurements on methane-ethane mixtures                                          |         |      | → |
| Examine the prospects for new experiments on heats of mixing and virial coefficients of selected binary mixtures |         |      |   |

1. Title. Survey of Current Literature on LNG and Methane.  
Principal Investigator. Neil A. Olien
2. Cost Center Number. 2750362
3. Sponsor Project Identification. American Gas Association Project BR 50-10.
4. Introduction. It is important that all NBS personnel working in LNG, as well as the AGA and others, keep up with what is going on throughout the world in the LNG field. This project is designed to provide the Current Awareness and other information services to allow workers to keep abreast of new research and other developments.
5. Objectives or Goals. We will publish and distribute each April, July, October and January a listing of all significant papers, reports and patents relating to methane and LNG properties and technology. The references will be listed under convenient subject headings. The Quarterly will be distributed to all interested AGA member companies and be made available to the general public on a subscription basis. In addition, LNG related information will be entered into the Cryogenic Data Center's Information System for quick retrieval. A continuing awareness of the current publication scene will be maintained for any new periodicals to be reviewed cover-to-cover. Finally we will update and make available comprehensive bibliographies on the properties and technology of LNG. There are three bibliographies involved: methane properties, methane mixtures properties, and processes and equipment involving methane and LNG. These three will be updated each October.
6. Background. In 1969 we made a thorough review of the world's publications to determine which periodicals and abstracting services should be scanned cover-to-cover to adequately encompass the LNG field. The result is that we now scan over 300 primary publications and nearly 30 secondary publications. Of these approximately one-third are directly related to LNG. In addition, within the past year we have increased our coverage of the energy field to include hydrogen as a future fuel. Much of this information is also pertinent to LNG and as such is listed in our LNG-related publications. Our Current Awareness Service has been published weekly since 1964 and the Liquefied Natural Gas Survey has been published quarterly since 1970.

7. Program and Results. Two issues of the LNG Quarterly were prepared and distributed. There are now 118 subscriptions going to AGA Member Companies and 191 to other subscribers. In September and October we updated the three bibliographies covering methane properties, methane mixtures properties and processes and equipment involving methane and LNG.

For some time we have realized that the above mentioned comprehensive bibliographies had grown to such a large size as to limit their usefulness (e. g. , B-965 covering processes and equipment listed over 1500 references). With this in mind we have reviewed the individual references in each bibliography and selected those which were most useful either from the standpoint of accuracy of the data or the appropriateness of the subject matter. These are now complete and copies have been printed and are available for sale as listed below.

- B-1055 THERMOPHYSICAL PROPERTIES OF METHANE - A SELECTED BIBLIOGRAPHY, 61 pp. , indexed by property, phase and author (Sept. 1973) \$8.00.
- B-1056 PROPERTIES OF METHANE MIXTURES - A SELECTED BIBLIOGRAPHY, 95 pp. , indexed by property, system and author (Sept. 1973) \$10.00.
- B-1075 PROCESSES AND EQUIPMENT INVOLVING LIQUEFIED NATURAL GAS AND METHANE - A SELECTED BIBLIOGRAPHY, 52 pp. , indexed by subject and author (Oct. 1973) \$5.00.

During the period January through July 1974 we have distributed 32 copies of these and the comprehensive bibliographies.

8. Problem Areas. We have no problem areas at this time.

9. Funding. January 1 - June 30, 1974

|             |         |
|-------------|---------|
| Labor       | 7.5 K\$ |
| Other Costs | 2.1 K\$ |
| Total       | 9.6 K\$ |
| Remaining   | 8.0 K\$ |

10. Future Plans. Issue 74-2 of the LNG Quarterly was mailed to the National Technical Information Service for printing and distribution on June 19, 1974. Issue 74-3 will be published in late September or early October. The three bibliographies discussed in Item 7 above will be updated in October.

|                              | July | Aug. | Sept. | Oct. | Nov. | Dec. |
|------------------------------|------|------|-------|------|------|------|
| Search of Current Literature |      |      |       |      |      | →    |
| Preparation of Issue 74-3    |      |      | →     |      |      |      |
| Preparation of Issue 74-4    |      |      |       |      |      | →    |



1. Title. THERMOPHYSICAL PROPERTIES DATA FOR PURE COMPONENTS OF LNG MIXTURES  
  
Principal Investigators. R. D. Goodwin, G. C. Straty
2. Cost Center Number. 2750364
3. Sponsor. American Gas Association, Project BR50-10
4. Introduction. This cost center will provide comprehensive accurate thermophysical properties data to support the development of LNG technology at NBS and throughout the fuel gas industry.
5. Objectives or Goals. The objective of our work is the determination of comprehensive accurate thermophysical properties data for the major pure components (methane, ethane, propane, butanes, and nitrogen) of liquefied natural gas mixtures at temperatures between 90 K and 300 K and at pressures up to 350 atm (5000 psi). Our goal is to provide a range and quality of data that will be recognized as definitive or standard for all foreseeable low temperature engineering calculations.

Accurate phase equilibrium, compressibility, and thermodynamic properties data are needed to design and optimize gas separation and liquefaction processes and equipment. Accurate data for the pure components of LNG mixtures will permit developing calculation methods which take into account the dependence of the thermophysical properties on the composition.

6. Background. Liquefied natural gas is expected to supply an increasing percentage of the United States' energy requirements. It is likely that massive quantities of liquefied natural gas will be imported during the years 1976-1990. Ships and importation terminals are being built for transporting, storing, and vaporizing liquefied natural gas for distribution. Accurate physical and thermodynamic properties data for compressed and liquefied

natural gas mixtures are needed to support these projects. For example, accurate compressibility and thermodynamic properties data are needed to design and optimize liquefaction and transport processes; accurate data for the heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition, are needed to provide a basis for equitable custody transfer.

Accurate thermodynamic properties data for liquefied gas mixtures must be based on precise compressibility and calorimetric measurements; compressibility data give the dependence of thermodynamic properties on pressure and density (at fixed temperatures); calorimetric data give the dependence of thermodynamic properties on temperature (at fixed pressures and densities). It is impossible however, to perform enough compressibility and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation of the data to arbitrary compositions, temperatures and pressures. Instead, thermodynamic properties data for multicomponent mixtures usually must be predicted (extrapolated) from a limited number of measurements on the pure components and their binary mixtures.

This project was initiated to provide the natural gas industry with comprehensive accurate data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. We have published National Bureau of Standards Technical Note 653, Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar, by Robert D. Goodwin, during this reporting period. This report contains the most comprehensive and



accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating thermophysical properties data for LNG mixtures.

We have also published comprehensive accurate dielectric constant and Clausius-Mossotti function data for pure compressed and liquefied methane (Cryogenics 13, 712 (1973)). This data will provide a data base for mass and density gauging.

## 7. Program and Results.

### 7.1 Ethane, Thermodynamic Properties Data--R. D. Goodwin

We have completed a voluminous manuscript, "Provisional Values for the Thermodynamic Functions of Ethane," comparable with our report on methane in NBS Technical Note 653, "The Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar." The above ethane report covers the entire range of fluid states at temperatures from 90 to 600 K, and pressures to 700 bar. The purpose of this work has been twofold: to indicate those physical properties for which experimental data are inadequate; and to provide the AGA with useful results at an early date.

In this work on ethane we have achieved a long-sought goal, namely an equation of state for thermal computations of such simplicity that it virtually ensures a correct qualitative behavior of the  $P(\rho, T)$  surface and of the important derivatives, especially about the critical point. It also gives qualitatively acceptable extrapolation to pressures at least twice those of  $P$ - $\rho$ - $T$  data used for adjusting constants in the equation of state. A manuscript on the above unique equation of state has been

prepared for open publication. It is our hope that complex computations on LNG mixtures may be simplified by use of this equation in identical form for each pure component.

In appendices to the present report we give copies of our unpublished work on the physical properties of ethane, namely--

- |            |                                                                                                                        |
|------------|------------------------------------------------------------------------------------------------------------------------|
| Appendix J | R. D. Goodwin, The Vapor Pressure of Ethane, Laboratory Note 73-3, July 9, 1973.                                       |
| Appendix K | R. D. Goodwin, Ethane Virial Coefficients and Saturated Vapor Densities, Laboratory Note 73-4, Aug. 14, 1973.          |
| Appendix L | R. D. Goodwin, The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine, Laboratory Note 73-5, Sept. 18, 1973. |
| Appendix M | R. D. Goodwin, Liquid-Vapor Saturation Temperatures of Ethane and Methane, Laboratory Note 73-6, Nov. 28, 1973.        |

## 7.2 Ethane, Compressibility (PVT) Data -- G. C. Straty

In the gas expansion technique used in this laboratory for accurate, absolute, compressibility (PVT) determinations, the molar volume  $V$  of a cryogenic fluid contained in a cell at temperature  $T$  and pressure  $P$  is determined by expanding the fluid from the calibrated cell into large calibrated volumes maintained near room temperature ( $\sim 295$  K). Using the near-ideal-gas-like behavior of the room temperature gas, the number of moles of gas residing in the total system can be computed accurately. One of the factors limiting the accuracy of this method is the ability to assign correctly the appropriate proportions of the fluid to the cell and to the various noxious volumes elsewhere in the system.

PVT measurements on ethane present an additional problem not encountered with most cryogenic fluids such as methane, oxygen, etc., because the critical temperature of ethane (305.33 K) is well above room temperature. The consequence is that during many of the density measurements on ethane, relatively high density fluid would reside in external parts of the system which could not be accurately accounted for in the present apparatus without some modifications.

During this reporting period, appropriate portions of the apparatus have been enclosed in ovens and/or provided with heaters to maintain their temperatures well above the critical temperature of ethane. Thermometric sensors have been calibrated and installed to these various portions of the apparatus to enable the temperatures to be measured and accurate PVT data obtained. Volume calibrations of several new system components have been made. Preliminary testing of the apparatus has been performed with satisfactory results.

### 7.3 Methane, Sound Velocity Data -- G. C. Straty

The ultrasonic velocities of sound in pure saturated and compressed fluid methane have been measured at MHz frequencies. Data have been obtained along the saturation boundary from near the triple point to 186 K and along several isotherms from 100 K to 300 K at pressures up to about 345 bar. The sound velocity data have been combined with the previously measured PVT data to calculate the isentropic and isothermal compressibilities and the specific heat ratio  $C_p/C_v$ . Measurements along the compressed fluid isotherms at temperatures of 210 K and above were limited to a minimum density ranging from about 14 mol/l at 210 K to about 10 mol/l at 300 K due to the large sound attenuation in methane. A manuscript reporting the results of the ultrasonic sound velocity measurements on methane has been published in *Cryogenics*, 14, 367 (1974), and is attached as an appendix to this report.

A newly constructed light scattering spectroscopy apparatus has been employed to obtain hypersonic (GHz) velocity data at the lower densities where measurement by ultrasonic techniques were impossible. Preliminary data have been obtained to densities as low as 1 mol/l along several isotherms. Measurements in the regions of overlap with the ultrasonic data indicate excellent agreement, and overall agreement with calculated sound velocity data is satisfactory.

### 7.4 Methane, Thermophysical Properties Data

AGA Project BR50-10 was initiated to provide the natural gas industry with comprehensive accurate thermophysical properties data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. The final report of this work, "The Thermophysical Properties of Methane, From 90 to 50 K at Pressures to 700 Bar", was published as NBS Interagency Report (NBSIR) 73-342 in

October 1973. It has been reprinted as NBS Technical Note 653, by R. D. Goodwin, in April 1974. This report contains the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating accurate thermophysical properties data for LNG mixtures. (For example, see references [1 ] in the section on Densities of LNG Mixtures in this report.)

The NBS Cryogenics Division has suggested that the report should become internationally accepted as "agreed on" standard reference data by the American Gas Association, Inc., and the natural gas industry. This suggestion has received approval from the AGA Pipeline Research LNG Supervisory Committee and the AGA Measurement Committee and is currently under consideration by the AGA-LNG Committee, E. L. Smith, Chairman. The report was recently brought to the attention of the international LNG industry at the Fourth International Conference on LNG in Algiers, June 24-27, 1974 (see Paper VII-1 by L. A. Sarkes, AGA, Inc., and D. B. Mann).

8. Problem Areas. For ethane, the computation of an accurate thermodynamic network in liquid states is more difficult than for methane. Vapor pressure measurements of high accuracy are needed at low temperatures, where these pressures are so small that no accurate experimental technique so far has been developed. Heats

of vaporization are so large at low temperatures (17,000 J/mol) that the experimental error of greater than 1% in these data gives about 200 J/mol error in computations across the vapor liquid "dome." Densities of saturated liquid ethane in the mid-range of temperatures (160 to 250 K) apparently never have been measured. The melting line is known only with very low accuracy. Comparison of our calculated speeds of sound for saturated liquid ethane with experimental data suggests that derivatives of the  $P(\rho, T)$  surface (via the equation of state) are not as accurate at low temperatures as desired. All of these deficiencies suggest the need for new highly accurate compressibility ( $P$ - $\rho$ - $T$ ) measurements, sound velocity measurements in the homogeneous, single-phase domain, and possibly additional specific heat measurements, e. g.  $C_v(\rho, T)$ , over a wide range of  $(\rho, T)$ .

Some delays in the modifications of the PVT apparatus have been encountered and are due almost entirely to delivery delays of purchased components. This lost time however has largely been made up and the PVT program is essentially on schedule.

#### 9. Funding.

|                                       |           |
|---------------------------------------|-----------|
| Man-years Expended, January-June 1974 | 0.9       |
| Equipment and/or Services Purchased   | \$ 9.1 K  |
| Total Reporting Period Cost           | \$ 58.9 K |
| Balance Remaining (June 30, 1974)     | \$ 9.6 K  |



10. Plans for Future Work.

| Schedule                                          | 1974 |   |
|---------------------------------------------------|------|---|
|                                                   | 3    | 4 |
| Ethane:                                           |      |   |
| Complete editorial work on two major publications | →    |   |
| Measure compressibilities (PVT) of liquid ethane  |      |   |

1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES  
Principal Investigators. M. J. Hiza, W. M. Haynes, R. D. McCarty
2. Cost Center Numbers. 2751364, 2752364
3. Sponsor. LNG Density Project Steering Committee, American Gas Association, Inc., Project BR 50-11.
4. Introduction. Accurate density data for liquefied natural gas mixtures are needed to provide a basis for custody transfer methods and equitable custody transfer agreements. This project will provide a data base for developing accurate methods for mass and density gauging at NBS and throughout the fuel gas industry.
5. Objectives or Goals. The objectives of this work are to perform accurate (0.1%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures, mainly in the temperature range 90-150 K, at pressures to 10 bar; and to test and optimize accurate methods for calculating the densities of LNG mixtures at arbitrary compositions and temperatures. The basis for the custody transfer of natural gas is its heating value. It is difficult to determine and agree on the heating value of extremely large volumes of natural gas in the liquid state. Methods for calculating the heating value of liquefied natural gas require knowing its density, which in turn depends on its composition and temperature. As the compositions of LNG mixtures vary considerably depending on the source of the gas and the processing conditions, methods are needed for calculating accurate densities at arbitrary compositions and temperatures. The accuracy (0.1%) is important because of the extremely large volumes of liquid involved. Each 1% error in density is equivalent to an inequity of \$15-20 thousand dollars per shipload of LNG (72,000 m<sup>3</sup> class).



6. Background. This project is being carried out at NBS because of the realization that equitable custody transfer agreements could be reached more readily if the density measurements and the evaluation and development of calculation methods were performed by independent professionals of established reputation.

A high precision (0.05%) magnetic densimeter (based on Archimedes Principle) was designed and constructed prior to this reporting period.

7. Program and Results. Density measurements have been completed for nitrogen from 95 to 120 K, for methane from 105 to 160 K, and for ethane from 105 to 220 K. Some measurements on propane and on normal and isobutane have also been made.

The scope of work for this project has been amended (January 15, 1974) to include testing and optimizing of computer programs for calculating accurate (0.1%) density data for LNG at arbitrary compositions, temperatures and pressures in the following ranges:

Composition: more than 70% methane, less than 10%  
of each of the minor components.

temperature: 90-140 K.

pressures: below 10 bar

Funds for this work have been placed in cost center 2752364.

Calculation methods will be compared with accurate density measurements as they become available. Several available methods for predicting the densities of LNG mixtures have been programmed for the NBS digital computer. These methods include a cell model [1], a hard sphere model [2] a corresponding states technique [3] and a computerized graphical interpolation scheme [4].

8. Problem Areas. A potential problem area is the delay in delivery of accessory equipment for the mixture studies.

9. Funding.

2751364 (Measurements)

|                                        |           |
|----------------------------------------|-----------|
| Man years expended, January--June 1974 | 0.8       |
| Equipment and/or Services Purchased    | \$ 5.7 K  |
| Total Reporting Period Cost            | \$ 31.0 K |
| Balance Remaining (June 30, 1974)      | \$ 4.0 K  |

2752364 (calculation methods)

|                                       |           |
|---------------------------------------|-----------|
| Man years expended, January-June 1974 | 0.1       |
| Equipment and/or Services Purchased   | \$ 0.9 K  |
| Total Reporting Period Cost           | \$ 5.6 K  |
| Balance Remaining (June 30, 1974)     | \$ 14.5 K |

10. Plans for Future Work.

| Schedule:                                                                             | year<br>quarter | 1974 |   |
|---------------------------------------------------------------------------------------|-----------------|------|---|
|                                                                                       |                 | 3    | 4 |
| Measure densities of binary mixtures containing methane, ethane, propane and nitrogen |                 |      |   |
| Test available calculation methods                                                    |                 |      |   |

### References:

- [1] Albright, M. A., Technical Publication No. 3, A Report to the Gas Processors Assoc., 1812 First Place, Tulsa, Okla. 74103 (1973).
- [2] Rodosevich, J. B. and Miller, R. C., Paper No. K-5, Advances, in Cryogenic Engineering, Vol 18, (in press, 1974).
- [3] Mollerup, J. and Rowlinson, J. S., Chemical Engineering Science, 29, 1373 (1974).
- [4] Klosek, J. and McKinley, C., Proc. First Int. Conf. on LNG, Paper 22, Chicago (1968).

1. Title. Low Temperature Material Behavior  
Principal Investigators. R. P. Reed, R. L. Tobler, R. P. Mikesell, and R. L. Durcholz.
2. Cost Center Number. 2750430
3. Sponsor Project Identification. Maritime Administration Project 55-300-15-011.
4. Introduction. Data on thermal and mechanical properties of structural and insulation materials are essential to facilitate material selection on the basis of cost and safety. Proper material choice and reliable definition of material behavior using fracture mechanics is of major economic importance for cryogenic containers in the sea transport of LNG.
5. Objectives. The objective of this program is to obtain fracture toughness and fatigue crack growth rate data in the temperature range 76-300 K. These measurements are being conducted on a series of Fe-Ni alloys and Al alloys.
6. Background. To construct tanks for sea transport of LNG requires between 500,000 and 7,000,000 pounds of expensive alloys, depending on the type of tanker chosen. This large-scale consumption of costly alloys demands very careful material selection to insure economical but safe, storage tanks. Therefore, since MarAd's goal is to reduce ship costs, it is in their interest to insure the availability of relevant thermal and mechanical property data to enable the best possible material selection and dependable, efficient design.
7. Program and Results. The materials effort in this program has concentrated on two areas, a general materials properties assessment and the initiation of an experimental low temperature tensile, fatigue, and fracture study of candidate materials. The materials properties assessment has included a compilation of all fatigue and fracture data on Fe-Ni steels and their weldments, a collection of ship design data and an analysis of materials in use, an assessment of the current production and/or research efforts of the materials suppliers, an assessment of the current materials requirements for LNG containers by the American Bureau of Shipping, U.S. Coast Guard, and the ASME pressure vessel code, and the bibliography of literature containing data on aluminum alloys, non-metallics, and insulation materials. For the experimental program the materials were procured;

specimens were made for tensile, fatigue and fracture tests for selected materials; a variable temperature cryostat was built; and the experimental procedures proofed, and fracture data obtained on selected Fe-Ni alloys.

### Materials Properties Assessment

The literature data from some 60 references on the fatigue and fracture properties of the ferritic Fe-Ni steels ( $\text{Ni} < 18\%$ ) has been extracted, critically valuated, and compiled. The fracture data in the compilation are the impact energy; nil ductility transition, crack opening displacement, fracture toughness, and dynamic tear tests and their dependencies on temperatures, composition, and heat treating or cold working. Fatigue data include fatigue lifetime and fatigue crack growth rates at LNG temperatures. Also included are tensile properties, hardness, impact energies, explosion bulge tests, and other fracture data. The entire compilation will be sent as an inter-agency report and included in a review article on LNG materials in the open literature.

The production and research capabilities of the major suppliers of LNG structural alloys were also assessed. Direct contact was made with the research personnel of all the major suppliers to assess what work on these materials has been done or was in progress. These in-house efforts indicated are generally low level. We have attended the LNG Materials Conference at the British Welding Institute and visited Technigaz, Det Norske Veritas, and the Welding Institute to provide information about the foreign efforts in LNG materials research. We also have a member of our staff on the Cryogenic Materials for LNG Tank Applications Committee of the Metals Properties Council.

### Experimental Program

Test materials of 1-1/2 inch thick plate have been obtained for the 3-1/2, 5, 6 and 9% Ni steels and A $\ell$  5083. Fe-9Ni steel has been obtained from two sources.

A cryostat for variable temperature control near LNG temperatures was designed and built. The experimental procedures, especially J integral test techniques, were evaluated and proven satisfactory. New methods were devised to monitor the crack growth and crack opening.

Fracture toughness and fatigue crack growth rate tests at 300, 195, 111, 76, and 4 K have been completed. These alloys include Fe-6Ni and Fe-5Ni in the QLT or austenitized, temperized, and reversion annealed condition, and Fe-9Ni in the quenched and tempered condition.

Linear elastic fracture mechanics parameters ( $K_Q$ ,  $K_{IC}$ ) and J-integral ( $J_{IC}$ ) test data have been measured for identical 1.25 inch thick compact tensile specimens. For the first time valid  $K_{IC}$  critical stress intensity data have been obtained for these Fe-Ni alloys. Also, for the first time a decided temperature dependence of the fatigue crack growth rate has been measured; the rate of crack propagation is higher at 76 K compared to room temperature for all alloys.

#### Program Publications and Talks

One talk was presented at the ASTM Special Symposium on Properties of Materials for LNG Tankage. This conference was held in Boston, Mass. on May 21-22, 1974.

One paper will be included in the Special Technical Publication of that ASTM conference, "Low Temperature Fracture Behavior of Ferritic Fe-Ni Alloy Steels," by R. L. Tobler, et al. (see Appendix P).

8. Problem Areas. Testing has proceeded on schedule. There are no delays.
9. Funding. During this reporting period, about \$75,000 has been spent. This leaves \$40,000 for research during the next reporting period.
10. Future Plans. During the next three months the fatigue and fracture toughness properties of Fe-3-1/2Ni (heat treated), steel and 5083 Al will be measured at 300, 195, 111, and 76 K.



1. Title. Elastic Properties of Materials Intended for Use in Liquefied Natural Gas Applications  
Principle Investigators. H. M. Ledbetter, E. R. Naimon (NRC-NBS Postdoctoral Research Associate, 1973-74) and W. F. Weston (NRC-NBS Postdoctoral Research Associate, 1973-74).
2. Cost Center Number. 2750131
3. Sponsor Project Identification. NBS
4. Introduction. The elastic properties of structural and insulation materials must be known before such materials can be selected economically and safely. Proper material choice for cryogenic containers for the sea transport of LNG is a major economic problem.
5. Objectives. The objectives of this program were to determine the elastic properties of structural materials in the temperature range 4 - 300 K. These properties include: Young's modulus, shear modulus, bulk modulus, and Poisson's ratio. Measurements were made on a series of iron-nickel alloys and on some aluminum alloys.
6. Background. Depending on the type of tanker for sea transport of LNG, 500,000 to 7,000,000 pounds of expensive alloys are required. This large-scale consumption of costly metals demands careful material selection to insure economical, but safe, storage tanks. Since the goal is to reduce ship costs, it is essential to have relevant elastic property data for the best possible selection and design of tankers.
7. Program and Results. The program's general aspects, the experimental approach, the data analysis, and both tabulated and graphed results are given in a manuscript "Low-temperature elastic properties of aluminum 5083-0 and four ferritic nickel steels" by W. F. Weston, E. R. Naimon, and H. M. Ledbetter. This manuscript is included as Appendix N.
8. Problem Areas. Currently, there are no problems with the program.
9. Funding. The program cost is estimated at \$15,000.
10. Future Plans. Currently, no additional measurements are planned in this program.

1. Title. Heating Value of Flowing LNG  
Principal Investigators. J. A. Brennan and R. W. Stokes
2. Cost Center Number. 2750361
3. Sponsor Project Identification. Pipeline Research Committee  
(American Gas Association) PR-50-48.
4. Introduction. This project will draw on information and facilities generated by other sectors of the NBS LNG effort. Thus the calibration of a densimeter used will be traceable to the NBS density reference system being constructed by Younglove under cost center 2751361. Mixture density data produced under 2751364 by Haynes and Hiza will also provide a necessary input to the proper interpretation of results.
5. Objectives. The original objective of this program was to set up a LNG flow facility and to evaluate selected flowmeters in LNG service. In November 1973 the objective was expanded to demonstrate the accuracy of measurement of the heating value of LNG flowing in a pipeline through integration of state-of-the-art instrumentation for flow, density and heating value. The expanded project has been conceived of in a three year time frame. In the first year individual components will be calibrated and installed in the NBS LNG flow facility.
6. Background. The need for accurate flowmetering of LNG provided the original impetus for the work in this program (unpublished NBS Report [1972], NBSIR 73-300). Since liquid natural gas may be sold on the basis of heating value the program was broadened to include the necessary instrumentation for determining heating value of LNG, this expanded program to commence early in 1974. The objectives are based on scaling small flowmeters capable of laboratory testing up to full line size components. Appropriate intermediate sizes are included with field tests scheduled as part of the overall project.
7. Results. A four-inch vortex shedding flowmeter was purchased and calibrated in water at NBS-Gaithersburg over the flow range 50 to 600 gallons per minute. The results of the calibration agreed very closely with the manufacturers predicted performance. A liquid nitrogen calibration was run at NBS-Boulder over a reduced flow range of 50-230 gallons per minute. Since it is not possible to test the meter in the actual piping configuration that will be used later in the LNG tests, a second liquid nitrogen test will be run with a different inlet piping configuration to determine what affect the piping may

have on meter performance. The results of both tests will be compared with the results reported earlier [NBSIR 74-358] on the 1-1/2 and 2-inch meters to see if the performance is similar.

A new sensor was supplied with the four-inch meter which did not require changing when changing test fluids from water to liquid nitrogen. It was still necessary to adjust the current through the sensor but this adjustment is easily made.

A second four-inch vortex shedding flowmeter was obtained from a different manufacturer and calibrated in water at NBS-Gaithersburg. This meter is now being tested in the liquid nitrogen flow facility at NBS-Boulder. Results of the liquid nitrogen test are now being analyzed.

Test results from both four-inch meters will be used in testing techniques for predicting meter performance in liquid nitrogen. Testing of the second four-inch meter was not originally planned as part of the test program but the availability of a meter using the same principle but with different sensing elements was thought to be a worthwhile addition to the program. The additional testing required will add some expense to the program but the information available is already proving very beneficial.

All the components are on hand to fabricate the test section necessary for the LNG field tests on the four-inch meter. This section will be fabricated and ready for installation in July 1974. No installation date at the LNG facility has been determined at this time.

Static tests on the densitometer have been completed. Tests were run in liquids methane, propane and nitrogen using the same densitometer that had previously been tested in flowing liquid nitrogen on another program. Some adjustments to the electronics were necessary before testing in liquid methane but after the adjustment was made the densitometer worked properly in all three fluids.

It was decided to delay the purchase of new densitometers for this phase of the program until some additional information from the LNG Density Reference System is available. With that information selection of the most desirable densitometer should be easier. Since the older densitometer was available no program delay or other adverse affects will result from this decision.

The densitometer was intended to be used over small temperature limits but was used in these tests over the range 78 K to 277 K. Results obtained on each fluid independently were consistent but when all results were combined there was a definite degradation in overall

performance. This degradation appears to be caused by covering such a broad temperature range with an instrument not designed for that use. Discussions have been held with the manufacturer about the performance and much of the above analysis came from that discussion. Since actual LNG measurements will not involve such wide temperature limits this problem should not occur in actual usage.

A surplus calorimeter was obtained from one of the sponsoring companies and some preliminary tests run. As a result of these tests and discussions with the manufacturer it was decided to have the manufacturer's service representative inspect the machine. The service representative suggested what would be needed to put the machine in good operating condition and the necessary parts have been ordered. Approximately \$700 will be expended to refurbish the calorimeter.

A surplus trailer has been obtained and will be installed at the LNG flow facility for housing the calorimeter. After installation the trailer will require some renovation for proper calorimeter operation.

A gravitometer has been ordered and is scheduled for delivery the end of July. This gravitometer will be installed in the trailer with the calorimeter.

The two-inch flowmeter and the densitometer have been installed in the LNG flow facility in preparation for system integration tests. Installation of the calorimeter must await the trailer installation and refurbishing work.

In preparation for the system tests the electrical circuitry for the load cell system has been modified in an effort to improve performance. The flow control valve has also been modified for better control at low flow rates.

8. Problem Areas. No problems have been encountered that would have an adverse affect on the project.

9. Funding.

|                              |          |
|------------------------------|----------|
| Man Years Expended           | 0.75     |
| Major Equipment Purchased    | \$ 5,776 |
| Total Reporting Period Costs | \$45,000 |
| Balance on Hand              | \$31,000 |

10. Future Plans. Flowmeter tests at an LNG peak shaving plant are planned late this calendar year. Actual test date depends on facility availability. The calorimeter will be refurbished and installed at the LNG flow facility after the necessary building arrangements have been completed. After the calorimeter is running, system integration tests will be started. It is planned to complete this phase of the program this calendar year.



1. Title and Principal Investigators. LNG Density Reference System - Ben Younglove.
2. Cost Center Number. 2751361
3. Sponsor Project Identification. American Gas Association, Inc. Project BR 50-10.
4. Introduction. The emphasis of the LNG effort of NBS is in providing technical support to industry in meeting the energy needs of our economy with natural gas.

The density reference system will evaluate the ability of commercially available instruments to measure densities of LNG. Density is an essential measurement in performing total energy content determinations of natural gas reservoirs. While this effort is oriented towards metrology, the output from cost center 2751364 will provide basic reference data on pure liquids and mixtures which will serve as density standards.

5. Objectives. This research will provide a system for evaluating density measurement capability of commercially available meters. We will evolve a density reference system capable of generating accurate densities for this evaluation. From the commercial meters we will attempt to select one capable of performance as a transfer standard in order to provide traceability of accuracy to field density measurement systems.

The first year will be devoted to construction and testing of the density reference system. In the second year we will concentrate on evaluation of commercial meters, while the final year will involve selection testing and application of the transfer standard.

6. Background. In early 1973 a proposal was made to the American Gas Association for research in several areas of LNG technology to be done at this installation. Part of this program was the density reference system. Initial scheduling indicated for the first year of work, starting in April to be design, fabrication, and testing of a density system. Work actually commenced in August as a result of staffing difficulties. Since this initiation, we have conducted extensive study on the feasibility of various techniques for such a system, deciding finally on an application of Archimede's principle (see 7. below). Construction has begun on the various components of the system, and the automatic weighing head plus a precision gas balance for mixture determination are on order.



7. Program and Results. Two sample containers were built. A large one of approximately 8.9" O. D. x 17" deep is intended to house, at best, all of the densimeters that are anticipated. Another of the same diameter, but 7" deep will be used for preliminary testing and can also be used to house all but the largest of the densimeters. These vessels have been pressure tested to 200 psi at room temperature with water and the smaller has been pressure tested in liquid nitrogen to 90 psi with He gas.
- A vacuum jacket large enough to house the pressure vessels was obtained.
- A room temperature pressure vessel large enough to house the weighing head has been built and pressure tested to 200 psi with water. Various other items have been built such as vapor pressure bulbs and electrical feed throughs. The boule of single crystal silicon, donated by Texas Instruments, was cut to provide a buoy of approximately 127 grams and the ends polished. This will be suspended from the weighing head via fine tungsten wire.
- Manufacturers of densimeters have indicated willingness to loan working devices for test. One device is on hand and another is expected in about two weeks. Others will arrive later, the latest date mentioned for delivery was September this year.
8. Problem Areas. The weighing head being supplied by the manufacturer did not arrive during this reporting period. It is expected that this will be integrated in the system within the next two months.
9. Funding.
- |                        |          |
|------------------------|----------|
| Man Year Expended      |          |
| Principal investigator | 0.85     |
| Technician             | 0.31     |
| Equipment Purchased    | \$ 8,000 |
| Total Cost             | \$70,300 |
| Balance on Hand        | \$ 9,700 |
10. Future Plans. First three months. Continue assembly of density reference system. Install weighing head. Check ability of density monitor to measure water density at room temperature. Check system ability to provide reduced temperatures. Check system temperature regulation. Check density monitor performance with liquid nitrogen.

We will develop a test plan which will determine the statistical relevance of the experimental procedure.

Second three months. Install one or more test densimeters, depending on availability etc., and observe overall performance of density reference system with densimeters. Observe preliminary behavior of test densimeters.

1. Title. Liquefied Natural Gas Technology Transfer  
Principle Investigator. D. B. Mann
2. NBS Cost Center. 2750401
3. Sponsor Project Identification. Maritime Administration, Project 55-330-15-011.
4. Introduction. The NBS support of the Maritime Administration (MarAd) LNG ship program is divided into two area contract. These are an experimental program (NBS Cost Center 2750430) and the subject cryogenic technology transfer. In addition to those objectives listed below this program provides a cohesive structure for the coordination of the NBS LNG program.
5. Objectives. Cryogenic Technology Transfer is designed to provide cryogenic technical information, data, and advice to the Maritime Administration (MarAd), its contractors and other agencies performing work of interest to, or for, MarAd in the design, development testing, construction and operation of LNG ships and ship components.
6. Background. The Merchant Marine Act of 1970 restructured federal maritime policies to make bulk carrier vessels, such as tankers and LNG ships, eligible for construction and operating subsidies. In December 1973 the keel was laid for a 926 foot long LNG vessel carrier at Quincy, Mass. The keel laying initiated the construction of the first LNG tanker to be built in the United States. American ship builders have orders for a total of 13 of these complicated ships. Various future projections indicate a total of from 25 to well over a 100 ships will be required to handle LNG importation within the next 10-15 years. LNG marine technology is presently foreign dominated. As a matter of fact, many of the ships being constructed in U.S. shipyards are using designs under license from foreign industrial groups or governments. LNG is a cryogenic fluid and the massive technology developed over the past 15-20 years in cryogenics as applied to industrial gases and the aerospace effort provides a resource which could be applied profitably to improving the U.S. competitive position in the construction and operation of LNG shipping. Because of its historical association with broad based cryogenic technology over a period of 20 years, the NBS Cryogenics Division was requested to provide support to the MarAd LNG ships program in order to aid in the transfer of cryogenic technology where it could enhance the effectiveness of maritime LNG shipping. Therefore, on April 17, 1973 we submitted a work statement which was confirmed by the establishment of a program in May.

7. Program and Results. (1 January to 30 June, 1974) In the initial phases of the LNG Cryogenic Technology Transfer program emphasis was placed on establishing the level and degree to which we could interface with MarAd, MarAd research centers (NMRC), and MarAd contractors. Progress therefore is measured as specific responses to MarAd and MarAd contract requests and NBS generated output felt necessary for the overall program.

7.1. Data and Information - LNG. On March 5, 1975, N. A. Olien, Acting Chief of the NBS Cryogenic Data Center visited the National Maritime Research Center at Galveston, Texas for the purpose of surveying the information and library needs of the center. It was his purpose to provide NMRC aid and assistance in establishing a reference library for subjects dealing with liquefied natural gas. Mr. Olien spent some time with Tom Burttschell, Superintendent of Documentation Services at NMRC discussing how best to accomplish the task. Discussions were productive and upon returning to Boulder, Mr. Olien sent the following items to Mr. Burttschell of NMRC:

- 1) Six bibliographies on the properties of construction materials.
- 2) A bibliography on LNG refrigeration utilization.
- 3) A bibliography on the properties of methane and one on methane mixtures.
- 4) Two copies of the LNG technology bibliography.
- 5) A list of books on cryogenic subjects.
- 6) A list of LNG related periodicals with ordering information for each.
- 7) A copy of Goodwin's NBSIR 73-242 "Thermophysical Properties of Methane".
- 8) Two copies of the quarterly Hydrogen - Future Fuel.

It is believed that the necessary contacts have been made between NBS Boulder and NMRC Galveston which should result in a continuing exchange of information on the general subject of LNG.

7.2. LNG Custody Transfer Systems. NBS has been requested to review a custody transfer system to be installed on one of the ships constructed in U. S. shipyards and dedicated to LNG service. The request for review came from the ship owner through the ship contractor. NBS notified the Maritime Administration of the request with the recommendation that the review be performed under this Maritime funded program. After several iterations, a work statement

was submitted to the ship contractor outlining a two-phase work statement to accomplish the custody transfer review. The purpose of phase 1 - System Design Review - is twofold:

- 1) To estimate the total uncertainty of the shipboard measurement of LNG mass.
- 2) To suggest a possible testing program which would verify the design review.

The scope of work of phase 1 will entail the definition of technical areas which have direct bearing on the estimate of total uncertainty in the shipboard measurement of LNG mass. These areas will include, but not be limited to:

- a) Physical dimension of system components
- b) Changes in physical dimensions due to thermal contractions.
- c) Tank strapping procedures.
- d) Relationship between capacitance measurements, dielectric constant, liquid level and density.
- e) Range of LNG mixture fractions.
- f) Heat transfer and system thermodynamics.

It is expected that technical evaluations by the instrumentation subcontractor have already been performed in many of these areas, in these cases NBS will review the technical content of these valuations.

From the technical areas indicated above, it is expected that NBS will define a set of parameters which can be used to give a measure of the uncertainty in total mass. A mathematical relationship will then be derived for the total mass uncertainty in terms of these parameters. Limits on these parameters can then be set by NBS (or other users) giving the best information available. In this format, variations in system dimension from tank to tank can easily be incorporated in a total shipboard analysis.

Phase 2 - Physical Hardware Evaluation (Testing Program) - will not be initiated until the completion of phase 1.

Approval of the NBS work statement by General Dynamics was received on June 11 and authorization by MarAd to commit funds to the program was received on June 24. It is estimated that Phase 1 of the program will require 4 months for completion with the results being submitted to the sponsor in the form of an NBSIR.



7.3. Fourth International Conference on Liquefied Natural Gas. Dr. R. H. Kropschot and D. B. Mann of the Cryogenics Division of NBS attended the above conference held in Algiers, Algeria (23 June to 27 June 1974). LNG4 is the fourth in a series of conferences sponsored by the International Gas Union (IGU), London; the International Institute of Refrigeration (IIR), Paris; and the Institute for Gas Technology (IGT), Chicago. LNG4 was held in Algeria by invitation of the Algerian Gas Union and the Algerian Government. All conference meetings were convened at the Palace of Nations, situated in the Club des Pins just outside the capitol of Algiers. Technical tours to industrial areas containing LNG liquefaction sites were also provided. Dr. Kropschot and Mr. Mann, in addition to attending all sessions of the conference, toured the Skikdka industrial zone which includes the 450 million cubic feet per day liquefaction plant and port facilities.

During the opening session an address "The Role of Liquefied Natural Gas in U. S. Energy Policy" by Mr. John N. Nassikas, Chairman of the Federal Power Commission, seemed at first to indicate an official aloofness on the part of the U. S. in respect to large LNG programs such as those involving Algeria and other Arab countries. A study of Mr. Nassikas' press release of his address does not confirm this impression. Although he does indicate energy self-sufficiency as the U. S. policy and outlines the methods to be used in accomplishing this goal, he nevertheless indicates imports of LNG are estimated to be 3 trillion cubic feet by 1985 with an estimated investment of \$5 to 10 million in LNG. This is consistent with the AGA prediction of supplemental LNG import requirements of 2.7 trillion cubic feet by 1985 and 3.2 trillion cubic feet by 1990.

Mr. Louis A. Sarkes, Associate Director of the American Gas Association, Incorporated and Douglas Mann of the NBS Cryogenics Division co-authored a paper "A Survey of LNG Technological Needs in the U. S. - 1974 to 2000". Mr. Sarkes made the presentation which described the gas industry long range research plan and the current level of LNG research at NBS. The paper was well received and comments following the presentation indicated satisfaction on the part of delegates that the U. S. does have a structured plan for providing necessary research for continued U. S. participation in national and international LNG programs. (See Appendix O.)

Delegates (1900) from over 24 different countries, in addition to Algeria, were present at the conference with the U. S., France, Germany, Japan, and the United Kingdom representing the largest number of delegates in that order. This group of delegates assembled to attend a conference on a high technology industry that has matured



over the past few years to a point where large expansion can and is taking place. They, the delegates, want assurance that fixed expansion will take place, they wish to be part of this expansion, they wish to identify who is responsible for the present program in Algeria, and to assess the political climate of this first of the Arab states to embark on a massive program of export of natural gas in liquid form.

The delegates found a demonstrated desire on the part of the government, both in policy and structure, to encourage input of foreign technology for expansion of their program in LNG and a demonstrated desire to show a stable political structure to accomplish this. The Algerian operating personnel had a pride in their workmanship and their progress and are working definitely towards technological self-sufficiency, independent of all foreign influences. It seems that their position is rather strong in that they feel that they can dedicate over 100 trillion cubic feet of natural gas reserves for possible LNG export projects. This should be compared with the north slope of Alaska estimated reserves of 26 trillion cubic feet which could possibly enter the LNG export trade.

Fifty-two papers were presented covering such subjects as world trade in LNG, large-scale transportation projects, liquefaction and processing, peak load plants and liquid handling, marine transportation, storage systems, new developments, and economic and legal aspects. Papers were printed and distributed in a bound proceedings. In spite of the tone of the subjects listed there did not seem to be a great deal of new technology, only improvements.

8. Problem Areas. Major problem areas under this program are the definition of scope and content. MarAd has a number of separate current advisory studies, the results of which are necessary for defining their position in LNG marine technology. Until these decisions by MarAd are made, NBS will continue to provide information and assistance of the type outlined above.

9. Funding. January 1 - June 30, 1974.

|             |              |
|-------------|--------------|
| Labor       | \$67,000     |
| Other Costs | <u>3,000</u> |
| Total       | \$70,000     |
| Remaining   | \$42,000     |

The major portion of the remaining funding will be expended during the next 4 months on the custody transfer review. NBS will continue

to provide consultation and advisory services in the transfer of LNG technology within the scope and present funding limitations.

1. Title. Federal Power Commission Consultation  
Principle Investigators. D. B. Chelton and A. F. Schmidt
2. Cost Center Number. 2750404
3. Sponsor. Federal Power Commission - Bureau of Natural Gas --  
letter agreement dated 4 June 1973.
4. Goals. The Cryogenics Division will provide consultation and advisory services to the Federal Power Commission on the cryogenic safety and the design aspects of several current applications before the FPC for authorization of LNG terminal and storage facilities. These services cover properties of cryogenic environments, insulation systems, cryogenic safety, thermodynamics, heat transfer, instrumentation and cryogenic processes such as refrigeration and liquefaction.
5. Background. Cost Center initiated July 7, 1973.
6. Program and Results. The results and status of those facilities presently under the jurisdiction of the Federal Power Commission and subject to our review are outlined in the following table.

Elements of the facilities that are subject to review are the land-based cryogenic storage tank components, bounded by the tanker or barge, the vaporizer and the liquefaction units (if any). These include, but are not limited to the transfer lines, the storage tanks, the vaporizers and the process piping as it interacts with the storage tanks. It is essential that the reviews cover the operation, maintenance and emergency procedural philosophies for each terminal. Based upon these studies, reports are submitted to the staff of the FPC setting forth the technical evaluations and conclusions on each proposal. In addition, NBS may provide expert witnesses on behalf of the staff of the FPC in any hearings on the aforementioned applications.

Emphasis is placed on the safety aspects of the facilities including their possible interactions with the surrounding areas. The impact of engineering design such as appropriate use of existing technology and material selection for structural integrity must be assessed. The basis of review includes various codes and standards. prior experience, precedent and engineering knowledge.

7. Funding.

|                                 |          |
|---------------------------------|----------|
| Total Funding FY 74             | \$57,000 |
| Expenses July 1 - June 30, 1974 | \$57,000 |
| Man Years of Effort             | 1.0      |

8. Future Plans. At the present time there are several pending applications, but detailed information is not yet available. It is anticipated that additional facilities will be reviewed as applications are made to the Federal Power Commission.

FPC CONSULTATION - LNG FACILITY REVIEW

| Applicant                           | Location          | Type Facility           | Storage Facility                         | Site Tour | Technical Meeting | Status     |
|-------------------------------------|-------------------|-------------------------|------------------------------------------|-----------|-------------------|------------|
| Distrigas - New York Terminal       | Staten Island, NY | Import Terminal         | 2-900,000 barrel                         | 8/21/73   | 8/21/73           | Complete   |
| Distrigas - Everett Marine Terminal | Everett, MA       | Import Terminal         | 1-600,000 barrel<br>1-374,000 barrel     | 8/23/73   | 8/23/73           | Complete   |
| Algonquin LNG, Inc.                 | Providence, RI    | Import Terminal         | 1-600,000 barrel                         | 8/24/73   | 8/24/73           | Complete   |
| Northern Natural Gas Co.            | Carlton, MN       | Peak Shaving            | 1-630,000 barrel<br>10.8 MMCFD liquefier | 10/30/73  | 10/30/73          | Complete   |
| Northwest Pipeline Corp.            | Plymouth, WA      | Peak Shaving            | 1-348,000 barrel<br>6.0 MMCFD liquefier  | 10/31/73  | 10/31/73          | Complete   |
| East Tennessee Natural Gas Co.      | Kingsport, TN     | Peak Shaving            | 1-348,000 barrel<br>5.0 MMCFD liquefier  | **        | 11/29/73          | Complete   |
| Transco Terminal Co.                | Bridgeport, NJ    | Import Terminal         | 3-600,000 barrel                         | 1/23/74   | 1/23/74           | Complete   |
| Southern Energy Co.                 | Savannah, GA      | Import Terminal         | 4-400,000 barrel                         | 1/24/74   | 2/6/74            | Complete   |
| Alabama-Tennessee Natural Gas Co.   | Greenbrier, AL    | Peak Shaving            | 1-117,000 barrel<br>2.0 MMCFD liquefier  | **        | 2/5/74            | Complete   |
| Trunkline LNG, Inc.                 | Lake Charles, LA  | Import Terminal         | 3-600,000 barrel                         | 2/7/74    | 5/14/74           | In process |
| Chattanooga Gas Co.                 | Chattanooga, TN   | Peak Shaving            | 1-348,000 barrel<br>10.0 MMCFD liquefier | 2/28/74   | 2/28/74           | Complete   |
| Tennessee Natural Gas Co.           | Nashville, TN     | Peak Shaving            | 1-290,000 barrel<br>5.0 MMCFD liquefier  | 2/27/74   | 2/27/74           | Complete   |
| Pacific Indonesia                   | Port Hueneme, CA  | Import Terminal         | 2-550,000 barrel                         | 5/15/74   | *                 | In process |
| Northern Natural Gas Co.            | Hancock Co., IA   | Peak Shaving            | 1-630,000 barrel<br>10.8 MMCFD liquefier | *         | *                 | In process |
| Texas Eastern Transmission Company  | Staten Island, NY | Peak Shaving/<br>Import | *<br>9.0 MMCFD liquefier                 | *         | *                 | In process |

\* to be determined

\*\* NBS visit not scheduled

1. Title. LNG - Dual Fuel Auto  
Principle Investigator. J. M. Arvidson
2. Cost Center Number. 2750590 (Reimbursable)
3. Sponsor Identification. Joint NBS and General Services Administration  
Requisition Number F4KE023, Case Number 66551.
4. Introduction. The work described relates to the general area of transfer of technology based on Division experience in the handling of liquefied combustible gases, instrumentation and systems analysis.
5. Objectives. To establish the degree of hazard to passengers and auto on the release of liquefied natural gas in the trunk area of the standard GSA dual fuel (natural gas and gasoline) sedan.
6. Background. The General Services Administration (GSA) dual fuel automobiles are equipped to run on gasoline or natural gas. In the initial GSA program the natural gas was compressed and carried in high pressure cylinders, which in sedans were located in the trunk space. To take care of accidental leakage, a large vent was installed in the roof of the passenger compartments, with two small air vents installed in the top of the trunk space. More recently, most of the dual fuel installations have been installed with liquefied natural gas (LNG) carried in an insulated tank at low pressure in the trunk compartment.

Natural gas has a density less than air and therefore is buoyant and will rise at temperatures above about 151 K. It was anticipated that vents provided would be adequate for dilution of explosive concentrations of methane gas in the trunk and passenger compartments under conditions of operation. This was believed to be the case even if very cold gas was vented (at a temperature of less than 157 K) as the amount of the methane gas vented at this lower temperature would be minimal, would be heated rapidly above 157 K and then vented normally.

A recent explosion of a sedan, believed to be caused by migration of methane gas from a trunk area to the passenger area, raised the question of the functional adequacy of the high level vents. In other words, can a combustible mixture of cold methane gas (at a temperature of less than 157 K) migrate from a leakage area in the trunk to the passenger compartment, and if so, can additional venting, relocation of vents, or other methods be incorporated in the sedan to eliminate this hazardous situation?



GSA has requested the Cryogenics Division of NBS to perform tests, analyze data, and make recommendations for the modification (if any) to be made in the vent system or any other aspect, method or design that would minimize the concentration of methane gas (or LNG vapor) in the trunk or passenger area to well below the lower explosion limit (at least to 50% LEL).

A test program and results were described in the previous reporting period (NBSIR 74-358). The potentially hazardous condition caused by release of methane or vaporized LNG in the trunk area was reported to the co-sponsor in the form of a progress report.

7. Program and Results. Review of the test reports is in progress by sponsor.

A decision by GSA is expected by September on the future course of the program. Permission was requested of GSA and granted for NBS to start hydrogen gas venting studies.

8. Problem Areas. None

9. Funding. No expenditures this reporting period.

10. Future Plans. NBS submitted a preliminary work statement to GSA for further work designed to define the limits of venting capability of the sedan (by minor structural changes) and acquire venting data of this type of car body with hydrogen gas. In addition, a safety review of LNG distribution stations (gas stations) was proposed.

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## APPENDIX A

## VISCOSITY OF SATURATED LIQUID METHANE<sup>‡</sup>

W.M. HAYNES<sup>#</sup>

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Received 27 June 1973

### Synopsis

The results of absolute measurements of the viscosity of saturated liquid methane using a torsionally vibrating quartz crystal are reported for temperatures from 95 to 190 K. Comparisons are made with other data, all of which have been obtained with techniques different from that of the present work.

The viscosity of saturated liquid methane has been determined at temperatures from 95 to 190 K, and at densities from 0.2 to 0.45 g/cm<sup>3</sup> with a torsionally oscillating quartz cylinder. The precision and accuracy of these measurements are estimated to be better than 0.5 and 2%, respectively. Details of the apparatus and experimental techniques have been given in a previous publication<sup>1)</sup>.

The sample gas was obtained from commercial, research-grade methane. Mass-spectral analysis of a representative sample by the supplier resulted in a specified minimum purity of 99.97 mol percent. Its most probable impurities were nitrogen, carbon dioxide, and ethane. The sample gas was further purified by passing it through a silica-gel trap immersed in an ice bath.

Absolute measurements of the viscosity–density product were accomplished using a quartz crystal of approximately 5 cm length and 0.5 cm diameter. (Its exact dimensions and mass have been reported in an earlier paper<sup>1)</sup>.) Densities were obtained from measured temperatures and an equation developed by Goodwin and Prydz<sup>2)</sup> to represent their liquid densities along the saturation curve. In general, the equation represented experimental density data within the 0.1% uncertainty of their measurements, except within a few degrees of the critical temperature. At 190 K the density may be in error by as much as 0.5%.

The present results are presented in table I as a function of temperature and density; in fig. 1 the experimental points are plotted as a function of temperature along with independent measurements<sup>3–9)</sup> of other laboratories. The older and, generally, less consistent data<sup>6–9)</sup> are included for the sake of completeness.

<sup>‡</sup> Contribution of the National Bureau of Standards (USA), not subject to copyright.

<sup>#</sup> NRC-NBS Postdoctoral Research Associate, 1970–72.



TABLE I

| Viscosity of saturated liquid methane |                                 |                                                  |
|---------------------------------------|---------------------------------|--------------------------------------------------|
| Temperature<br>(K)                    | Density<br>(g/cm <sup>3</sup> ) | Viscosity<br>( $\mu\text{g/cm s}$ ) <sup>‡</sup> |
| 95.000                                | 0.44581                         | 1784                                             |
| 100.000                               | 0.43902                         | 1569                                             |
| 105.000                               | 0.43208                         | 1383                                             |
| 110.000                               | 0.42497                         | 1225                                             |
| 115.000                               | 0.41766                         | 1090                                             |
| 120.000                               | 0.41013                         | 975                                              |
| 125.000                               | 0.40235                         | 883                                              |
| 130.000                               | 0.39429                         | 810                                              |
| 135.000                               | 0.38591                         | 733                                              |
| 140.000                               | 0.37715                         | 673                                              |
| 145.000                               | 0.36793                         | 612                                              |
| 150.000                               | 0.35819                         | 557                                              |
| 155.000                               | 0.34779                         | 514                                              |
| 160.000                               | 0.33659                         | 465                                              |
| 165.000                               | 0.32437                         | 419                                              |
| 170.000                               | 0.31077                         | 376                                              |
| 175.000                               | 0.29523                         | 343                                              |
| 180.000                               | 0.27658                         | 309                                              |
| 185.000                               | 0.25174                         | 261                                              |
| 190.000                               | 0.20020                         | 198                                              |

<sup>‡</sup> 1  $\mu\text{g/cm s}$  =  $10^{-7}$  Pa s.

It is particularly satisfying that the discrepancies between the values obtained with four different techniques (this work; oscillating disk, ref. 3; capillary flow, ref. 4; falling cylinder, ref. 5) are generally within the estimated uncertainties of the independent measurements. It should be noted that the results of refs. 4 and 5 were acquired on viscometers calibrated with fluids of presumably known viscosity.

The agreement of the present saturated-liquid results for methane with those of refs. 3 and 4 is consistent with comparisons of saturated-liquid data for argon<sup>1,3,4</sup>) and oxygen<sup>4,10,11</sup>) obtained with the same apparatuses by the respective authors. However, it should be mentioned that, for compressed liquid argon and oxygen, the results obtained with the present apparatus<sup>1,10</sup>) showed a consistently larger pressure dependence than those obtained with the oscillating-disk viscometer of Hellemans *et al.*<sup>3,11</sup>). (The discrepancies are most significant at the higher liquid temperatures, *e.g.*, approximately 20% at 10 MN/m<sup>2</sup> at 140 K for argon<sup>1</sup>).) The above inconsistency is pointed out to illustrate that, although viscosity measurements by different experimenters on the same fluid may agree for the saturated liquid, it does not necessarily follow that this agreement would carry over to the compressed liquid or other fluid regions.

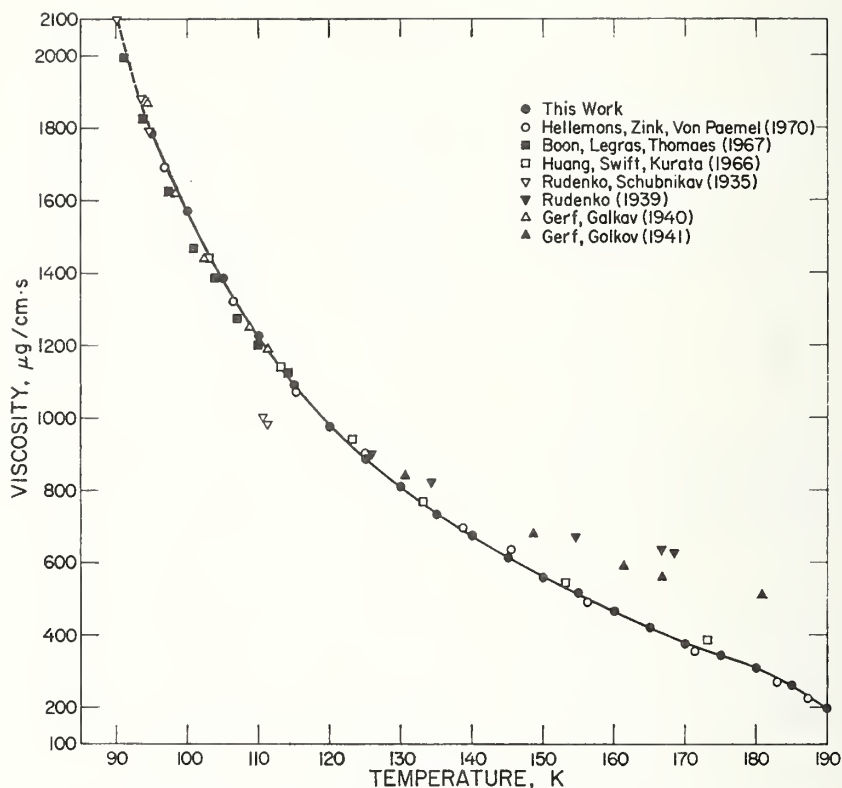


Fig. 1. Viscosity of saturated liquid methane; data from this work and refs. 3-9.

**Acknowledgment.** The author would like to acknowledge the National Research Council, National Academy of Sciences – National Academy of Engineering and the National Bureau of Standards for the Postdoctoral Research Associateship during the tenure of which this research was performed.

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## APPENDIX B

*This report gives accurate interpolation functions for the Clausius–Mossotti functions (molar polarizabilities) of pure compressed gaseous and liquid methane, ethane, propane, butanes and nitrogen; and suggests a method for calculating the dielectric constants or the densities of their mixtures. The accuracy of calculated Clausius–Mossotti functions for mixtures containing a high concentration of methane is expected to be better than 1% using only data for the pure components. Additional data for the dependence of the excess Clausius–Mossotti function on composition could reduce the uncertainty in Clausius–Mossotti functions for multicomponent mixtures to less than 0.2%.*

R-809

## The Clausius–Mossotti functions (molar polarizabilities) of pure compressed gaseous and liquid methane, ethane, propane, butanes, and nitrogen

D. E. Diller

Accurate thermophysical properties data for compressed and liquefied gases and their mixtures are needed to design liquefaction, storage, and transportation processes and to provide a basis for custody transfer agreements. For example, accurate Clausius–Mossotti function data for compressed and liquefied natural gas mixtures are useful for practical *densimetry applications*; the density of a multicomponent fluid mixture can be determined directly from a dielectric constant measurement (or vice versa). The compositions of technically important gas mixtures are so variable however that it is nearly impossible to obtain sufficiently comprehensive experimental data for many applications. Instead, accurate thermophysical properties data for multicomponent mixtures must usually be calculated from data for the pure components and selected binary mixtures.<sup>1, 2</sup> The purpose of this report is to give accurate interpolation functions for the dielectric constants and Clausius–Mossotti functions of pure compressed and liquefied methane, ethane, propane, butanes, and nitrogen in a form useful for calculating the dielectric constants or densities of their mixtures.

### Interpolation functions for the Clausius–Mossotti functions of pure compressed gaseous and liquid methane, ethane, propane, butanes, and nitrogen

The Clausius–Mossotti function (molar polarizability),

$$C-M \equiv \frac{\epsilon - 1}{\epsilon + 2} V \quad (1)$$

gives a relationship between the dielectric constant  $\epsilon$  and the molar volume  $V$  of a non-polar fluid. For low density gases, the Clausius–Mossotti function is related to the molecular polarizability  $\alpha$  by

$$C-M = \frac{4\pi}{3} N_0 \alpha \quad (2)$$

where  $N_0$  is Avogadro's number; therefore  $C-M$  depends mainly on a fixed molecular property of the fluid. The Clausius–Mossotti function for many non-polar gases and liquids has been found to be nearly independent of temperature, pressure, density, and state; varying less than 2% over large density and temperature ranges. The Clausius–Mossotti functions for compressed non-polar gases typically increase slightly with increasing density, reaching a maximum in the vicinity of the critical density, and then decreasing continually with further increasing density. The Clausius–Mossotti functions for most non-polar fluids decreases slightly with increasing temperature at fixed densities. Accurate empirical representation of the complete dependence of the Clausius–Mossotti functions of compressed gases and liquids on density and temperature is a difficult problem. An accurate 'equation of state' for the Clausius–Mossotti function is not available, even for the simplest pure gases. The dependence of  $C-M$  on density (neglecting the dependence on temperature) is given to good approximation however by

$$C-M \simeq A_\epsilon + B_\epsilon \rho + C_\epsilon \rho^2 + D_\epsilon \rho^3 + \dots \quad (3)$$

The coefficient  $B_\epsilon$  is analogous to the second virial coefficient in the pressure virial expansion; the coefficients  $C_\epsilon$  and  $D_\epsilon$  are purely empirical. The coefficients for (3) have been obtained for pure compressed and liquefied methane, ethane, propane, butanes, and nitrogen from available dielectric constant and density data. Further discussion of the data basis and the coefficients obtained for (3) is given for each fluid.

**Methane.** Accurate data for the dielectric constants and densities of pure compressed and liquefied methane are given in references 3 and 4. Data are available for temperatures between 91 and 373.4 K at pressures to 345 bars. The data for the low density limit  $A_\epsilon$  and the liquid–vapour equilibrium curve have been fitted to (3). The coefficients obtained for (3) are given in Table 1. The uncertainty in the Clausius–Mossotti function for pure methane calculated with these coefficients is probably smaller than 0.2%.

**Ethane.** Accurate data for the dielectric constants and densities of pure gaseous and liquid ethane at temperatures

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Table 1 The Clausius–Mossotti functions for pure compressed and liquefied methane, ethane, propane, butanes, and nitrogen

|                  | Coefficients for (3)<br>$A_E, \text{cm}^3 \text{mole}^{-1}$ | $B_E, (\text{cm}^3 \text{mole}^{-1})^2$ | $C_E, (\text{cm}^3 \text{mole}^{-1})^3$ | $D_E, (\text{cm}^3 \text{mole}^{-1})^4$ |
|------------------|-------------------------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| Methane          | 6.541 <sup>4†</sup>                                         | 8.52 <sup>3</sup>                       | $-4.26 \times 10^2$ <sup>3</sup>        | $+4.43 \times 10^3$ <sup>3</sup>        |
| Ethane           | 11.22 <sup>5</sup>                                          | 20.00 <sup>5</sup>                      | $-14.60 \times 10^2$ <sup>5</sup>       |                                         |
| Propane          | 15.93 <sup>5</sup>                                          | 76.00 <sup>5</sup>                      | $-58.40 \times 10^2$ <sup>5</sup>       |                                         |
| <i>n</i> -butane | 20.65 <sup>6</sup>                                          | 141.00 <sup>*7</sup>                    | $-139.20 \times 10^2$ <sup>*7</sup>     |                                         |
| <i>i</i> -butane | 20.88 <sup>6</sup>                                          | 143.00 <sup>*7</sup>                    | $-99.00 \times 10^2$ <sup>*7</sup>      |                                         |
| Nitrogen         | 4.389 <sup>8</sup>                                          | 2.20 <sup>8,9</sup>                     | $-1.00 \times 10^2$ <sup>9,10</sup>     |                                         |

\* Obtained from refractive index measurements

† Reference numbers

between 283 and 305 K at densities up to twice the critical density are given in reference 5. The Clausius–Mossotti function for compressed fluid ethane changes less than 1% with density and temperature in this range. Coefficients for (3) are given in reference 5 and are reproduced in Table 1. It is expected that the Clausius–Mossotti function obtained by extrapolating (3) to densities up to  $3\rho_c$  at temperatures down to 90 K will be accurate to about 0.5%.

**Propane.** Accurate data for the dielectric constants and densities of pure gaseous and liquid propane at temperatures between 293 and 369.5 K at densities to  $2\rho_c$  are also given in reference 5. Coefficients obtained for (3) are given in reference 5 and reproduced in Table 1. If (3) is extrapolated to densities up to  $3\rho_c$  and temperatures down to 90 K, the estimated uncertainty in  $C-M$  will be smaller than 1%.

**Normal and isobutane.** Accurate data for the dielectric constants and densities of pure gaseous normal and isobutane at temperatures above 400 K are given in reference 6. There are no dielectric constant data available for liquefied butanes at low temperatures, but accurate data for the refractive indices of gaseous and liquid normal and isobutane along the liquid–vapour equilibrium curve are given in reference 7. The coefficients  $B_n$  and  $C_n$  obtained for the dependence of Lorentz–Lorentz function,  $(n^2 - 1/n^2 + 2) \times V$ , on density are given in Table 1. The uncertainty in  $C-M$  obtained by using  $A_E$ ,  $B_n$ , and  $C_n$  in (3) is probably smaller than 1%.

**Nitrogen.** Accurate data for the dielectric constants and densities of compressed gaseous and liquid nitrogen at temperatures between 65 and 313 K are given in references 8, 9, 10. The Clausius–Mossotti function for gaseous and liquid nitrogen changes less than 1% with density and temperature in this range. Coefficients are given for (3) for nitrogen in Table 1. The uncertainty in  $C-M$  calculated for nitrogen using (3) with these coefficients is probably smaller than 0.5%.

#### Suggested method for calculating the Clausius–Mossotti functions (and dielectric constants or densities) for mixtures of compressed and liquefied gases

If the Clausius–Mossotti function,

$$C-M_{\text{mixture}} \equiv \frac{\epsilon_{\text{mixture}} - 1}{\epsilon_{\text{mixture}} + 2} \times V_{\text{mixture}} \quad (4)$$

is known for a liquefied non-polar gas mixture, then the dielectric constant can be determined from a density measurement, or the density  $\rho \equiv 1/V$  can be determined from a dielectric constant measurement. The Clausius–Mossotti function can be calculated for a multicomponent fluid mixture by using

$$C-M_{\text{mixture}} = \sum_i x_i C-M_i + C-M^E(x_i, T, P) \quad (5)$$

where the  $x_i$  and  $C-M_i$  are the mole fractions and Clausius–Mossotti functions for the pure components and  $C-M^E$  is the excess Clausius–Mossotti function. The excess Clausius–Mossotti function is defined here as the change in  $C-M$  on mixing at fixed temperature and pressure. The excess Clausius–Mossotti function is zero for non-polar gas mixtures at low densities. There are no data available for the Clausius–Mossotti functions of liquefied gas mixtures. The excess Clausius–Mossotti function  $C-M^E$  is expected to be less than 1% of  $C-M_{\text{mixture}}$  for liquefied natural gas mixtures containing a high concentration of methane. Therefore calculations of  $C-M_{\text{mixture}}$  for liquefied natural gas mixtures are expected to be accurate to better than 1% using pure component data only. Accurate data for the dependence of  $C-M^E$  on composition could probably reduce the uncertainty in  $C-M_{\text{mixture}}$  to less than 0.2%.

I would like to thank G. C. Straty, R. D. Goodwin, and J. F. Ely for the use of their data before publication, and J. D. Olson for assistance with the calculations.

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## APPENDIX C

*A 33 term modified Benedict—Webb—Rubin equation of state is presented for methane. The adjustable parameters in the equation of state have been estimated using recent experimental data and least squares techniques which include the thermodynamic equilibrium conditions for the co-existing liquid and vapour phases. Comparisons of the new equation of state and an older modified Benedict—Webb—Rubin equation of state to experimental data are given.*

## A modified Benedict—Webb—Rubin equation of state for methane using recent experimental data

R. D. McCarty

There is currently an extensive worldwide interest in the properties of liquefied natural gas (LNG). This laboratory has recently completed an experimental programme on the thermodynamic properties of methane,<sup>4, 7</sup> the principal constituent of LNG. These new data are believed to be more accurate than those previously available and it therefore seemed worthwhile to use these new data to estimate the coefficients to a modified Benedict—Webb—Rubin (MBWR) type equation of state. The MBWR equation of state is especially appropriate for the study of the properties of mixtures for two reasons; first, the mathematical form of the equation allows the inclusion of the thermodynamic conditions for phase equilibria<sup>1, 2</sup> in the parameter estimation process, and second, the MBWR is widely used throughout the world for the calculation of the thermodynamic properties of other fluids. The particular form of the BWR modification used here was developed by Jacobsen<sup>6</sup> for nitrogen. The development of this equation by Jacobsen included a long and exhaustive study to determine an optimum functional form. The applicability of this form of the BWR to other fluids has since been demonstrated for oxygen by Stewart et al.<sup>9</sup> and for hydrogen by this author.<sup>8</sup> The only other modification of the BWR considered was the form used by Bender<sup>1</sup> for a number of gases including nitrogen and methane. Both the equations of state for nitrogen (Jacobsen and Bender) were constructed using the thermo-dynamic conditions for phase equilibria. The comparisons given later in this paper show that the form used by Jacobsen reproduces the new experimental data better than the form used by Bender. This result is not surprising as the form used by Jacobsen has 33 adjustable constants while the form used by Bender has 20 adjustable constants.

### Equation of state

The parameters  $N_1$ – $N_{32}$  for the equation of state, (1), were estimated by least squares techniques using the data listed in Table 1. The parameter  $\gamma$  was chosen such that  $\gamma\rho^2 \approx +1$  as suggested by Bender.<sup>1</sup>

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Table 1 Summary of data

| Reference | No of points | Temperature range, K | Saturation data | Density range, mole l <sup>-1</sup> | Kind of data         |
|-----------|--------------|----------------------|-----------------|-------------------------------------|----------------------|
| 4         | 555          | 92–300               | No              | 3–28.5                              | PVT                  |
| 10        | 274          | 92–300               | No              | 8–28                                | Cv                   |
| 4         | 200          | 91–190               | Yes             | 0.016–28.12                         | Orthobaric densities |
| 3         | 171          | 273–398              | No              | 0.75–12.5                           | PVT                  |
| 4         | 96           | 140–270              | No              | 0.5–2.0                             | PVT                  |
| 4         | 100          | 91–190               | Yes             | 0.016–28.12                         | Gibbs function       |

The saturation data listed in Table 1 were calculated from equations given by Goodwin,<sup>4</sup> see appendix. The condition of equal Gibbs function for the saturated liquid and saturated vapour in isothermal co-existence was included as data points at the 100 saturation temperatures referred to in Table 1. The equation of state was also constrained at the critical point to  $T = T_c = 190.555$  K,  $\rho_c = 10.23$  mole l<sup>-1</sup>,  $P = P_c = 45.387$  atm, and  $(\partial P/\partial \rho) \equiv (\partial^2 P/\partial \rho^2) \equiv 0$ . For a more detailed description of the techniques of simultaneous data fitting, constraints, and weighting see Hust and McCarty<sup>5</sup> or McCarty.<sup>7</sup> The functional form of the equation of state is

$$\begin{aligned}
 P = & \rho RT + \rho^2 (N_1 T + N_2 T^{1/2} + N_3 + N_4/T + N_5/T^2) \\
 & + \rho^3 (N_6 T + N_7 + N_8/T + N_9/T^2) \\
 & + \rho^4 (N_{10} T + N_{11} + N_{12}/T) + \rho^5 (N_{13}) \\
 & + \rho^6 (N_{14}/T + N_{15}/T^2) + \rho^7 (N_{16}/T) \\
 & + \rho^8 (N_{17}/T + N_{18}/T^2) + \rho^9 (N_{19}/T^2) \\
 & + \rho^3 (N_{20}/T^2 + N_{21}/T^3) \exp(-\gamma\rho^2) \\
 & + \rho^5 (N_{22}/T^2 + N_{23}/T^4) \exp(-\gamma\rho^2)
 \end{aligned} \quad (1)$$

$$\begin{aligned}
& + \rho^7 (N_{24}/T^2 + N_{25}/T^3) \exp(-\gamma\rho^2) \\
& + \rho^9 (N_{26}/T^2 + N_{27}/T^4) \exp(-\gamma\rho^2) \\
& + \rho^{11} (N_{28}/T^2 + N_{29}/T^3) \exp(-\gamma\rho^2) \\
& + \rho^{13} (N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4) \exp(-\gamma\rho^2)
\end{aligned}$$

where  $P$  is in atmospheres,  $\rho$  is in mole  $l^{-1}$ , and  $T$  is in kelvins. The coefficients ( $N_i$ ) are given in Table 2.

## Comparisons

The equation,

$$\text{Gibbs}(\rho_l, T) - \text{Gibbs}(\rho_v, T) = 0 \quad (2)$$

was formulated using the equation of state (1). Equation 2 was then solved for the co-existing saturated liquid and vapour densities ( $\rho_v$  and  $\rho_l$ ) at various temperatures ( $T$ ). The resulting  $P$ - $T$  locus is the vapour pressure curve given by the equation of state. Fig.1 compares the vapour pressures predicted by the equation of state to the vapour pressures given by Goodwin.<sup>4</sup>

Figs 2 and 3 show a comparison of the saturation densities using Goodwin's densities and values calculated by this equation of state and by Bender's equation of state, using the coefficients reported by Bender.

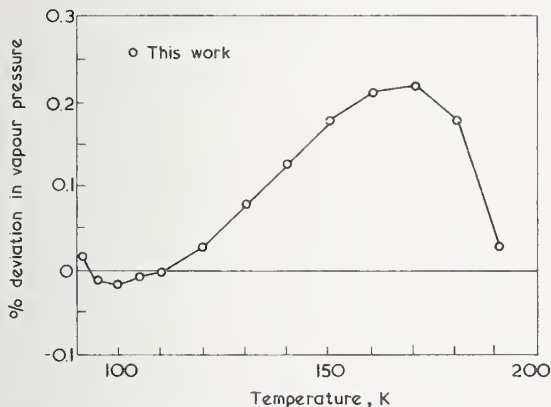


Fig.1 Comparison of vapour pressure predicted by the equation of state and those of Goodwin<sup>4</sup>

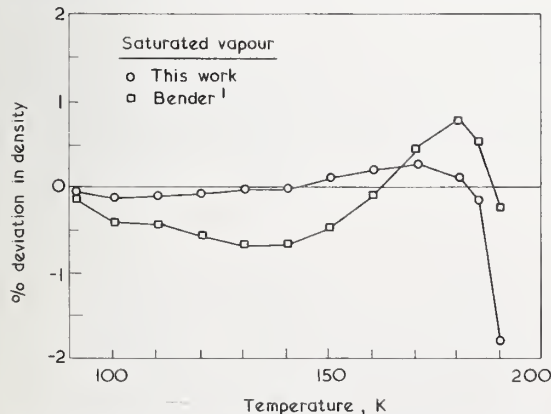


Fig.2 Comparison between saturated vapour densities of Goodwin<sup>4</sup> and those predicted by this equation of state and the equation of state by Bender<sup>1</sup>

Table 2 Coefficients to equation 1

|          |                                                      |
|----------|------------------------------------------------------|
| $N_1$    | $= -1.8439486666 \times 10^{-2}$                     |
| $N_2$    | $= 1.0510162064$                                     |
| $N_3$    | $= -1.6057820303 \times 10$                          |
| $N_4$    | $= 8.4844027562 \times 10^2$                         |
| $N_5$    | $= -4.2738409106 \times 10^4$                        |
| $N_6$    | $= 7.6565285254 \times 10^{-4}$                      |
| $N_7$    | $= -4.8360724197 \times 10^{-1}$                     |
| $N_8$    | $= 8.5195473835 \times 10$                           |
| $N_9$    | $= -1.6607434721 \times 10^4$                        |
| $N_{10}$ | $= -3.7521074532 \times 10^{-5}$                     |
| $N_{11}$ | $= 2.8616309259 \times 10^{-2}$                      |
| $N_{12}$ | $= -2.8685285973$                                    |
| $N_{13}$ | $= 1.1906973942 \times 10^{-4}$                      |
| $N_{14}$ | $= -8.5315715699 \times 10^{-3}$                     |
| $N_{15}$ | $= 3.8365063841$                                     |
| $N_{16}$ | $= 2.4986828379 \times 10^{-5}$                      |
| $N_{17}$ | $= 5.7974531455 \times 10^{-6}$                      |
| $N_{18}$ | $= -7.1648329297 \times 10^{-3}$                     |
| $N_{19}$ | $= 1.2577853784 \times 10^{-4}$                      |
| $N_{20}$ | $= 2.2240102466 \times 10^4$                         |
| $N_{21}$ | $= -1.4800512328 \times 10^6$                        |
| $N_{22}$ | $= 5.0498054887 \times 10$                           |
| $N_{23}$ | $= 1.6428375992 \times 10^6$                         |
| $N_{24}$ | $= 2.1325387196 \times 10^{-1}$                      |
| $N_{25}$ | $= 3.7791273422 \times 10$                           |
| $N_{26}$ | $= -1.1857016815 \times 10^{-5}$                     |
| $N_{27}$ | $= -3.1630780767 \times 10$                          |
| $N_{28}$ | $= -4.1006782941 \times 10^{-6}$                     |
| $N_{29}$ | $= 1.4870043284 \times 10^{-3}$                      |
| $N_{30}$ | $= 3.1512261532 \times 10^{-9}$                      |
| $N_{31}$ | $= -2.1670774745 \times 10^{-6}$                     |
| $N_{32}$ | $= 2.4000551079 \times 10^{-5}$                      |
| $\gamma$ | $= +0.0096$                                          |
| $R$      | $= 0.082056161 \text{ atm mole}^{-1} \text{ K}^{-1}$ |

The equation of state, (1), like other MBWR equations does not have the proper theoretical behaviour at the critical point, that is, the derivative  $(\partial^2 P / \partial T^2) \rho$  at the critical point does not become very large.

A comparison of experimental  $C_v$  with those calculated using (1) and those calculated by Bender's equation of state (coefficients from reference 1) is given in Fig.4. The large deviations between experimental  $C_v$ s and those calculated from Bender's equation were also noted in the case of  $O_2$ .

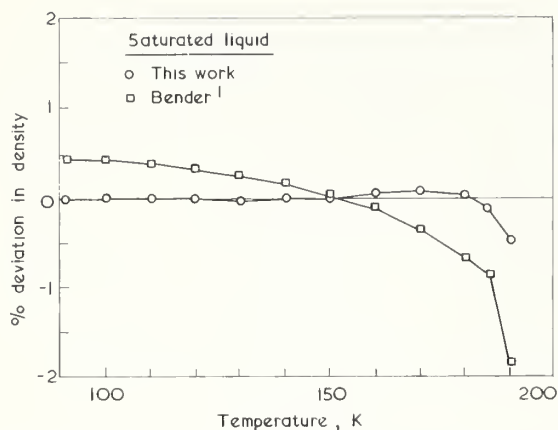


Fig.3 Comparison between saturated liquid densities of Goodwin<sup>4</sup> and the predictions of this equation of state and the equation of state by Bender<sup>1</sup>

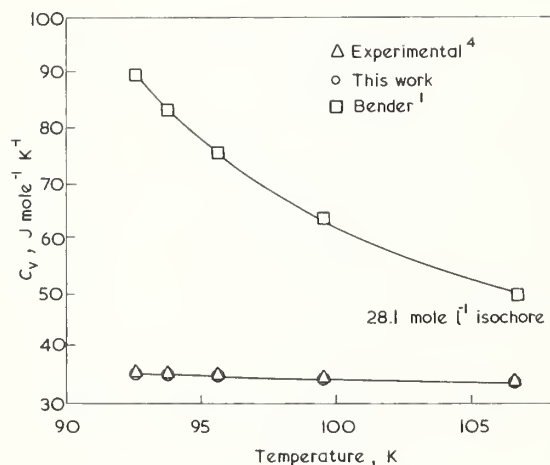


Fig.4 Comparison between experimental  $C_v$  data of Younglove<sup>9</sup> and predictions by this equation of state and the equation of state by Bender<sup>1</sup>

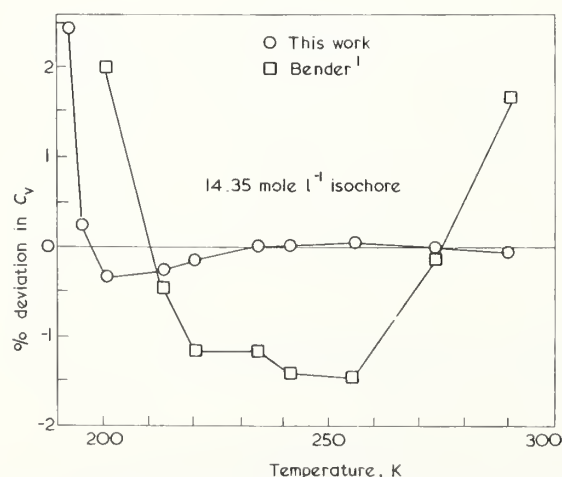


Fig.5 Comparison between experimental  $C_v$  data of Younglove<sup>9</sup> and predictions by this equation of state and the equation of state by Bender<sup>1</sup>

These large deviations between experimental  $C_v$ s and those calculated by Bender's equation of state occur only at low temperatures and high densities. Fig.5 gives a comparison of  $C_v$ s at moderate densities from the same three sources.

As is the case with all equations of state which cover a large range of pressure and temperature, the deviations between experimental and calculated densities become large in the region of the critical point. Fig.6 gives typical deviations between experimental and calculated densities from the same three sources.

The data points illustrated in the first six figures were chosen to show maximum deviations. A summary of the rms deviations is given in Table 3.

An attempt was made to use Bender's form of the modified BWR to represent the experimental data given in Table 1. Figs 7 and 8 compare the re-fitted Bender equation with (1) and experimental data. A comparison of Figs 4 and 6 with Figs 7 and 8 show a definite improvement in Bender's equation but also that it still does not represent the data as well as (1) does.

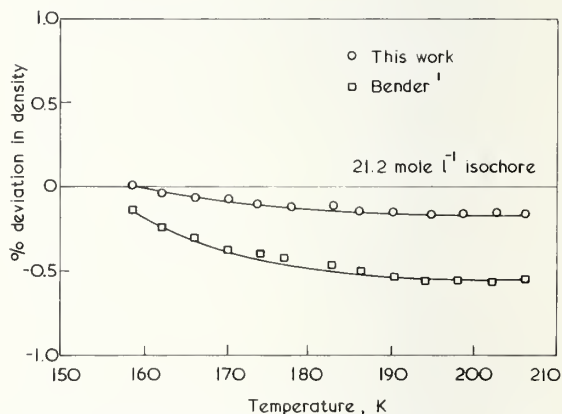


Fig.6 Comparison between experimental  $PVT$  data of Goodwin<sup>4</sup> and predictions by this equation of state and the equation of state by Bender<sup>1</sup>

Table 3 rms deviations between equation 1 and input data (Table 1)

| Reference | No of points | rms in density, mole l <sup>-1</sup> | rms in pressure, atm |
|-----------|--------------|--------------------------------------|----------------------|
| 4         | 555          | 0.024                                | 0.91                 |
| 9         | 274          |                                      | 0.211 <sup>†</sup>   |
| 4         | 200          | 0.004                                |                      |
| 3         | 171          | 0.012                                | 0.40                 |
| 4         | 96           | 0.0023                               | 0.023                |
| 4         | 100          |                                      | 0.011 <sup>*</sup>   |

\* rms is in the Gibbs function difference of the saturated liquid and vapour in the units of J mole<sup>-1</sup>

† rms is in  $C_v$  J mole<sup>-1</sup> K<sup>-1</sup>

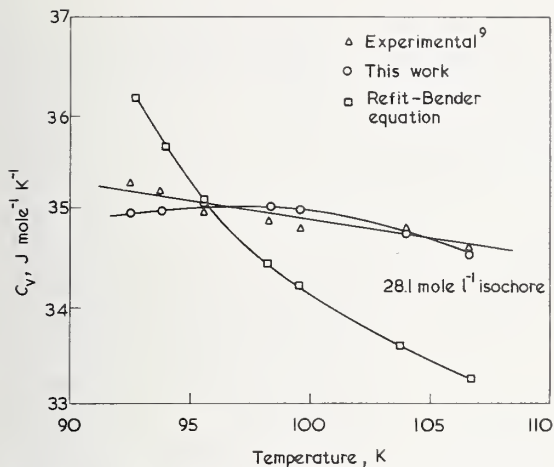


Fig.7 Comparison between experimental  $C_v$  data of Younglove<sup>9</sup> and predictions of this equation of state and a refit of Bender's equation of state

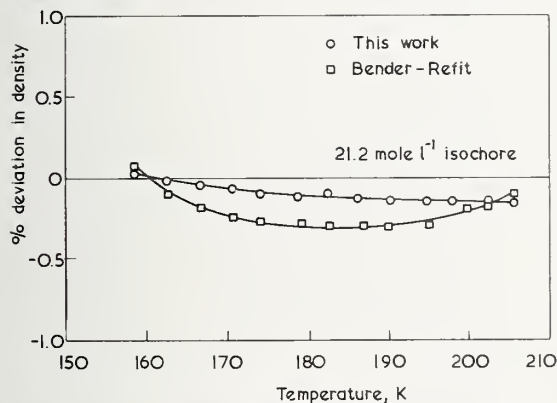


Fig.8 Comparison between experimental  $PVT$  data of Goodwin and predictions of this equation of state and a refit of Bender's equation of state

## Conclusion

From experience of estimating the constants for (1) for methane, the region of greatest uncertainty for (1) was found to be the densities of the saturated vapour boundary. More experimental data are needed before the uncertainty can be reduced.

The 33 term equation of state given here will reproduce the experimental data with greater accuracy than the form suggested by Bender, however, the 33 term equation requires double precision arithmetic on most digital computers and a much greater exponent range than the twenty term equation.

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## APPENDIX A

### Supplemental equations

To provide a useful minimum set of equations which will be helpful to the reader who wishes to programme the equation of state for the calculation of thermodynamic properties, the following equations from Goodwin<sup>4</sup> are reprinted here.

Vapour pressure equation

$$\log_e \frac{P}{P_t} = a x + b x^2 + c x^3 + d x(1-x)^{3/2} \quad (A1)$$

Equation for the saturated liquid densities

$$\frac{(\rho - \rho_c)}{(\rho_t - \rho_c)} = w^E \exp [A(1 - w^{2/3}) + B(1 - w^{4/3}) + C(1 - w^2)] \quad (A2)$$

Equation for the saturated vapour densities

$$\log_e \frac{\rho}{\rho_c} = a_1 w^{a_6} + a_2 w + a_3 w^{4/3} + a_4 w^{5/3} + a_5 U w \quad (A3)$$

Equation for the ideal gas  $C_v^0$

$$\frac{C_v^0}{R} = b_1 + \frac{4}{3} b_2 Q^{1/3} + \frac{5}{3} b_3 Q^{2/3} + 2 b_4 Q + b_5 \exp \left( \frac{b_6}{Q} \right) \left\{ \frac{b_6}{Q [\exp(b_6/Q) - 1]} \right\}^2 \quad (A4)$$

See Appendix B for the coefficients to equations A1, A2, A3, and A4.

## APPENDIX B

### Coefficients to equations

Table 4 Critical and triple point parameters for equations (A1, A2, A3, and A4)\*

|                                 |                                       |
|---------------------------------|---------------------------------------|
| $T_c = 190.55 \text{ K}$        | $\rho_c = 10.0 \text{ mole l}^{-1}$   |
| $T_t = 90.68 \text{ K}$         | $\rho_t = 28.147 \text{ mole l}^{-1}$ |
| $P_t = 0.117435675 \text{ bar}$ |                                       |

\*The critical density for equations A1, A2, A3, and A4 is slightly lower than the one used for the equation of state. The lower  $\rho_c$  is preferred by Goodwin,<sup>4</sup> but did not work well as a constraint for (1)



**Table 5 Coefficients to equation A1**

$$\begin{aligned}
 a &= 4.77748580 & c &= -0.56788894 \\
 b &= 1.76065363 & d &= 1.32786231 \\
 x &= (1 - T_t/T)/(1 - T_t/T_c)
 \end{aligned}$$

**Table 6 Coefficients to equation A2**

$$\begin{aligned}
 A &= -0.178860165 & C &= -0.01848987 \\
 B &= 0.04838475 & E &= 0.36 \\
 w &= (T_c - T)/(T_c - T_t)
 \end{aligned}$$

**Table 7 Coefficients to equation A3**

$$\begin{aligned}
 a_1 &= -2.7036003 & a_4 &= 5.2640362 \\
 a_2 &= 3.1661552 & a_5 &= -3.5269034 \\
 a_3 &= -8.6573409 & a_6 &= 0.46 \\
 w &= (T_c - T)/(T_c - T_t) & U &= (T_c/T - 1)/(T_c/T_t - 1)
 \end{aligned}$$

**Table 8 Coefficients to equation A4**

$$\begin{aligned}
 Q &= T/400 & b_5 &= 4.7207907 \\
 b_1 &= 2.5998981 & b_6 &= 5.02288 \\
 b_2 &= 1.4449418 & R &= 8.3143 \text{ J mole}^{-1} \text{ K}^{-1} \\
 b_3 &= -1.8472716 & T &= \text{in K} \\
 b_4 &= 0.8211218
 \end{aligned}$$

## APPENDIX C

### Sample calculations and table of symbols

**Table 9 Sample calculations from equations 1, A1, A2, A3, and A4**

For a temperature of 150 K and saturation pressure the equations 1 to A4 should give the following results.

|                 | (1)<br>Density,<br>mole l <sup>-1</sup> | (A1)<br>Pressure,<br>atm | (A2)<br>Density,<br>mole l <sup>-1</sup> | (A3)<br>Density,<br>mole l <sup>-1</sup> | (A4)<br>$C_v^0/R$ ,<br>dimensionless |
|-----------------|-----------------------------------------|--------------------------|------------------------------------------|------------------------------------------|--------------------------------------|
| Liquid<br>phase | 22.3223                                 | 10.278                   | 22.325                                   |                                          | 3.0053                               |
| Vapour<br>phase | 1.0187                                  | 10.278                   |                                          | 1.020                                    |                                      |

**Table 10 List of symbols**

|                           |                                                       |
|---------------------------|-------------------------------------------------------|
| $a, b, c, \text{ and } d$ | parameters to vapour pressure equation                |
| $A, B, C, \text{ and } D$ | parameters to equation for saturated liquid densities |
| $a_1, a_2 \dots a_6$      | parameters to equation for saturated vapour densities |
| $b_1, b_2 \dots b_6$      | parameters to equation for ideal gas $C_v^0$          |
| $P$                       | pressure                                              |
| $P_c$                     | critical pressure                                     |
| $P_t$                     | triple point pressure                                 |
| $R$                       | gas constant                                          |
| $T$                       | temperature                                           |
| $T_c$                     | critical temperature                                  |
| $T_t$                     | triple point temperature                              |
| $U$                       | reduced temperature in (A3)                           |
| $w$                       | reduced temperature in (A1)                           |
| $x$                       | reduced temperature in (A2)                           |
| $\gamma$                  | parameter in (1)                                      |
| $\rho$                    | density                                               |
| $\rho_c$                  | critical density                                      |
| $\rho_t$                  | triple point density                                  |



## APPENDIX D

# Properties Data for LNG

*A.G.A.-supported research seeks data essential to transport and exchange of this new energy source*

By D. E. DILLER  
Cryogenics Division  
Institute for Basic Standards  
National Bureau of Standards  
and  
L. A. SARKES  
Associate Director  
Research and Engineering  
American Gas Association

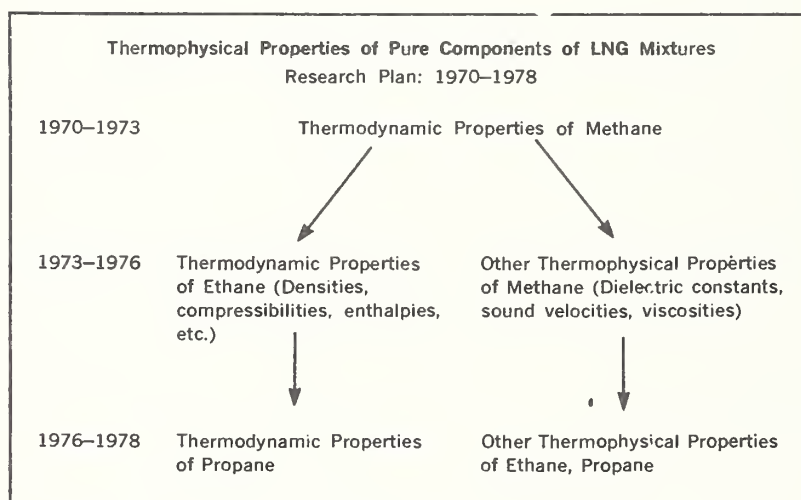


Table 1

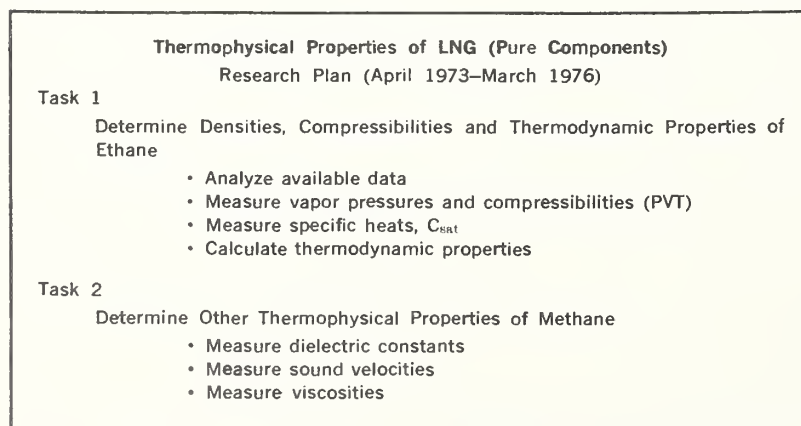


Table 2

Imported natural gas is supplying an increasing percentage of the nation's energy requirements and new technology is being developed to support large importation projects. To take advantage of the large volume decrease, about 600 to 1, which occurs when natural gas is liquefied, ships and importation terminals with cryogenic tanks are being built for transporting, storing, and vaporizing large quantities of liquefied gas.

To support these projects, extremely accurate data on physical and thermodynamic properties for liquefied natural gas mixtures is needed. For example, accurate compressibility and enthalpy data is essential to the design and optimization of liquefaction processes. To provide an equitable basis for transfer of custody, accurate data is needed for heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition.

There is little accurate data available on thermodynamic properties of liquefied natural gas mixtures at low temperatures. (Typical natural gas mixtures liquefy at temperatures below  $-120$  degrees F, boil at temperatures near  $-256$  degrees F, and freeze at temperatures below  $-296$  degrees F.)

Nor is there much accurate data available on thermodynamic properties of the liquefied pure components (methane, ethane, propane, etc.) in this temperature range. Moreover, the compositions of natural gas mixtures vary considerably from one source to another, and change continuously dur-

ing transport and storage due to selective vaporization.

The introduction of composition as an additional independent variable adds to the complexity of the task of providing an adequate data base.

Accurate data on thermodynamic properties of liquefied gases must be based on precise volumetric and calorimetric measurements. The dependence of the thermodynamic properties on pressure or density at fixed temperature is obtained from volumetric data. The dependence of these properties on temperature is determined by calorimetric measurements.

It is impossible to perform enough volumetric and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation in composition, temperature, and pressure. Instead, simple, accurate calculation methods are needed to predict thermophysical properties data for mixtures at arbitrary compositions, temperatures, and pressures from a minimum of measured input data (Note 1).

Several projects are underway currently at the Cryogenics Division of the National Bureau of Standards in Boulder, Colorado, to provide new input data for calculating the thermophysical properties of LNG mixtures.

One of these projects, supported directly by the American Gas Association, is obtaining accurate physical and thermodynamic properties data for the major pure components of LNG at temperatures down to -300 degrees F (90 K) and at pressures to 5000 psi. This range encompasses the combinations of temperatures and pressures most likely to be encountered in low temperature processes.

R. D. Goodwin and B. A. Younglove have developed accurate interpolation functions, computer programs, and data tables for all of the thermodynamic properties of gaseous and liquid methane at temperatures down to

296 degrees F. Methane is the most abundant major component of LNG with concentrations ranging from 80 to 99% in typical mixtures.

The NBS programs and data tables are based on precise measurements of the vapor pressures, densities, compressibilities, and specific heats performed at NBS and in other laboratories. Dr. Goodwin has developed an empirical equation of state for pure

methane which is consistent with all of the available volumetric and calorimetric measurements at temperatures between -296 degrees F and 400 degrees F at pressures to 10,000 psi.

Extensive comparisons have been made between the NBS data and the volumetric and calorimetric data from other laboratories. The NBS data will soon be available in both the Interna-

tional System of Units and British engineering units for the convenience of a variety of users.

The other project, supported by a consortium of natural gas companies in cooperation with A.G.A., will obtain accurate input data for calculating the densities of LNG mixtures. Accurate density data is urgently needed to provide a basis for equitable custody transfer. W. M. Haynes and M. J. Hiza are developing a magnetic densitometer, applying Archimedes principle, for precise density measurement on liquid mixtures in equilibrium with their saturated vapor. Measurements will be performed at temperatures between -200 degrees F and -295 degrees F at pressures to 250 psi to include the conditions likely to be encountered in transporting and storing LNG.

The priorities for continuing systematic work on these projects through 1975 have been tentatively established. Objectives of the work on pure components of LNG mixtures will be to provide accurate data on dielectric constants, speed of sound and viscosity for compressed gaseous and liquid methane, and to provide accurate thermodynamic properties data for compressed liquid ethane and propane at low temperatures. The LNG density project will provide accurate density data for saturated liquid methane, ethane, propane, butanes and nitrogen, and for selected binary and multicomponent liquid mixtures. New phase equilibrium data and low precision estimates of the heats of mixing will also be obtained. The density data will be used to develop and test methods for calculating the change in volume on mixing. ■

#### Note 1.

Several methods are available for calculating thermodynamic properties data for multicomponent liquid mixtures.<sup>1</sup> For liquid mixtures at temperatures well below the critical temperature, the "ideal mixture" is a useful concept. The molar volume and the molar enthalpy of an ideal liquid mixture are linear functions of the composition.

The only data required to calculate the properties of an ideal mixture are properties data for the pure components.

To calculate the properties of real liquid mixtures, one must add the small changes in the properties which occur in mixing. The following expressions give the recipe for calculating the volume and the enthalpy of a real liquid mixture:

$$\begin{array}{l} V \\ \text{real} \\ \text{mixture} \end{array} = \begin{array}{l} V \\ \text{ideal} \\ \text{mixture} \end{array} + V^R \quad (1)$$

$$\text{where } \begin{array}{l} V \\ \text{ideal} \\ \text{mixture} \end{array} = \sum_i x_i V_i$$

$$\text{and } \begin{array}{l} H \\ \text{real} \\ \text{mixture} \end{array} = \begin{array}{l} H \\ \text{ideal} \\ \text{mixture} \end{array} + H^R \quad (2)$$

$$\text{where } \begin{array}{l} H \\ \text{ideal} \\ \text{mixture} \end{array} = \sum_i x_i H_i$$

In these expressions the  $x_i$ , the  $V_i$ , and the  $H_i$  are the mole fractions, molar volumes, and molar enthalpies of each of the components. The  $V^R$  and  $H^R$  are the excess properties representing the property changes on mixing.

This calculation method separates the required input data into measurements of the physical properties of the pure components and measurements of the changes in the physical properties on mixing. Most of the information for the latter can be obtained from data on binary mixtures, i.e., pure components mixed two at a time.

<sup>1</sup> J. S. Rowlinson, *Liquids and Liquid Mixtures*, New York Plenum Press, second edition (1969)



## APPENDIX E

*Accurate measurements of the dielectric constant of methane have been made on the saturated liquid from near the triple point to 188 K and on the compressed fluid along selected isotherms from 100 K to 300 K and at pressures to 345 bar. The data are combined with accurate densities to obtain the molar polarizability and its dependence on density and temperature. The density range examined extends to nearly three times the critical density. The molar polarizability is found to increase initially with density and then decrease in qualitative agreement with theoretical predictions and the behaviour of other fluids.*

## Dielectric constant and polarizability of saturated and compressed fluid methane

G. C. Straty and R. D. Goodwin

In this paper, we present accurate, wide range measurements of the dielectric constant of saturated liquid methane from 91 K to 188 K and of compressed fluid methane along selected isotherms from 100 K to 300 K at pressures to 345 bar (1 bar =  $10^5$  N m<sup>-2</sup>). The data have been combined with accurate densities<sup>1</sup> to determine the molar polarizability and its dependence on density and temperature. The density range examined extends to nearly three times the critical density.

In the low density limit, the molar polarizability  $\theta$  is related to the dielectric constant  $\epsilon$  and density  $\rho$  via the Clausius–Mossotti relation

$$\theta = \left( \frac{\epsilon - 1}{\epsilon + 2} \right) \rho^{-1} = \frac{4\pi N_0 \alpha}{3} \quad (1)$$

where  $N_0$  is Avogadro's number and  $\alpha$  is the average molecular polarizability. The molar polarizability has been found to be very nearly independent of density for most non-polar fluids, often varying only a fraction of a percent over wide density ranges.<sup>2–5</sup> A knowledge of the polarizability can therefore be of practical value since it can provide a simple and convenient method for density determination through a measurement of capacitance. With increasing transport and handling of natural gas in the liquid state (LNG) a knowledge of the molar polarizability of liquid methane, the principal constituent of LNG, can be of particular importance since it offers a potentially useful method of LNG density metering.

As with other fluids,<sup>2–5</sup> the molar polarizability of methane shows small but significant deviations from (1). These deviations are usually analysed by expressing the polarizability in a truncated virial type expansion, that is,

$$\theta \equiv \left( \frac{\epsilon - 1}{\epsilon + 2} \right) \rho^{-1} = A_\epsilon + B_\epsilon \rho + C_\epsilon \rho^2 \quad (2)$$

where  $A_\epsilon = 4\pi N_0 \alpha / 3$  and  $B_\epsilon$  and  $C_\epsilon$  are the second and third dielectric virial coefficients. Existing theories<sup>6</sup> have yielded analytical expressions for these coefficients and wide range measurements of the dependence of the polarizability on density and temperature can be used to obtain information on molecular interactions.

### Experimental

The dielectric constant was determined by measuring the capacitance  $C$  of a highly stable cylindrical capacitor<sup>7</sup> with fluid contained between the plates. A subsequent measurement of the capacitance  $C_0$  of the evacuated capacitor then gives the dielectric constant directly as the ratio

$$\epsilon = \frac{C}{C_0}$$

The capacitances were measured using a commercial three terminal capacitance bridge capable of six figure resolution. Uncertainty in the measured dielectric constants is estimated at less than 0.005%. The methane used was 99.99% pure research grade and was passed through a molecular sieve to ensure no H<sub>2</sub>O was present. Temperatures were measured on the IPTS 1968 using a platinum resistance thermometer calibrated by the National Bureau of Standards. Pressures were measured by reference to oil pressures derived from an oil dead weight gauge accurate to within 0.01% through differential pressure transducers.<sup>8</sup> The experimental apparatus and procedures were identical to those used previously for measurements on oxygen and fluorine and have already been described in detail.<sup>4,5</sup>

### Results and discussion

The dielectric constants obtained for the saturated liquid are shown plotted against temperature in Fig. 1 and are tabulated along with the calculated polarizabilities in Table 1. Also shown for comparison are dielectric constants at the melting and boiling points obtained by Amey and Cole.<sup>9</sup> The dielectric constant for the critical point was calculated from an extrapolated value of the

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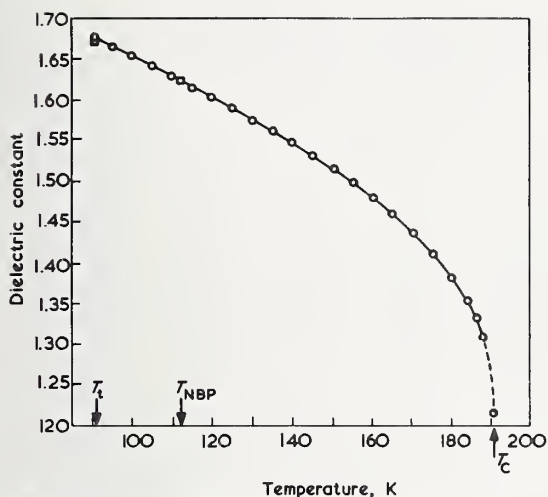


Fig.1 Dielectric constant as a function of temperature for saturated liquid methane  
 ○ this work; □ reference 9  
 Arrows indicate triple point, normal boiling point and critical point temperatures

polarizability of the saturated liquid from Fig.2. The polarizability at the critical density of  $10.10 \pm 0.1 \text{ mole l}^{-1}$  was taken as  $6.585 \pm 0.005 \text{ cm}^3 \text{ mole}^{-1}$  resulting in a calculated dielectric constant of  $1.2137 \pm 0.0025$  at the critical point.

The polarizabilities for the saturated and compressed liquid are shown plotted against density in Fig.2. The polarizability increases initially with density and then decreases in qualitative agreement with the behaviour of other fluids<sup>3,5</sup> and with theoretical prediction.<sup>6</sup> Data for the compressed fluid are tabulated in Table 2. The densities were calculated from the measured temperatures and pressures and the  $P\rho T$  data of Goodwin and Prydz<sup>1</sup>

Table 1. Dielectric constant and polarizability of saturated liquid methane

| $T$ ,<br>K | $\rho$ ,<br>$\text{mole l}^{-1}$ | $\epsilon$ | $\theta$ ,<br>$\text{cm}^3 \text{ mole}^{-1}$ |
|------------|----------------------------------|------------|-----------------------------------------------|
| 91.000     | 28.121                           | 1.67619    | 6.5410                                        |
| 95.000     | 27.789                           | 1.66668    | 6.5428                                        |
| 100.000    | 27.367                           | 1.65456    | 6.5448                                        |
| 105.000    | 26.934                           | 1.64225    | 6.5468                                        |
| 110.000    | 26.491                           | 1.62970    | 6.5488                                        |
| 115.000    | 26.035                           | 1.61688    | 6.5509                                        |
| 120.000    | 25.566                           | 1.60372    | 6.5527                                        |
| 125.000    | 25.081                           | 1.59024    | 6.5549                                        |
| 130.000    | 24.578                           | 1.57640    | 6.5574                                        |
| 135.000    | 24.055                           | 1.56204    | 6.5595                                        |
| 130.000    | 24.578                           | 1.57638    | 6.5572                                        |
| 135.000    | 24.055                           | 1.56204    | 6.5594                                        |
| 140.000    | 23.508                           | 1.54719    | 6.5621                                        |
| 145.000    | 22.933                           | 1.53167    | 6.5645                                        |
| 150.000    | 22.326                           | 1.51539    | 6.5669                                        |
| 155.000    | 21.678                           | 1.49819    | 6.5695                                        |
| 160.000    | 20.980                           | 1.47979    | 6.5718                                        |
| 165.000    | 20.219                           | 1.45992    | 6.5744                                        |
| 170.000    | 19.372                           | 1.43800    | 6.5766                                        |
| 175.000    | 18.401                           | 1.41319    | 6.5789                                        |
| 180.000    | 17.232                           | 1.38377    | 6.5816                                        |
| 184.000    | 16.036                           | 1.35418    | 6.5846                                        |
| 186.000    | 15.269                           | 1.33543    | 6.5864                                        |
| 188.000    | 14.260                           | 1.31117    | 6.5903                                        |
| 150.000    | 22.326                           | 1.51546    | 6.5677                                        |
| 175.000    | 18.401                           | 1.41329    | 6.5804                                        |
| 180.000    | 17.232                           | 1.38391    | 6.5838                                        |
| 184.000    | 16.036                           | 1.35430    | 6.5867                                        |
| 190.53*    | 10.10                            | 1.2137     | 6.585†                                        |

\*Critical point; the dielectric constant is calculated from an extrapolated value of  $\theta$

†Extrapolated value of  $\theta$ , see Fig.2

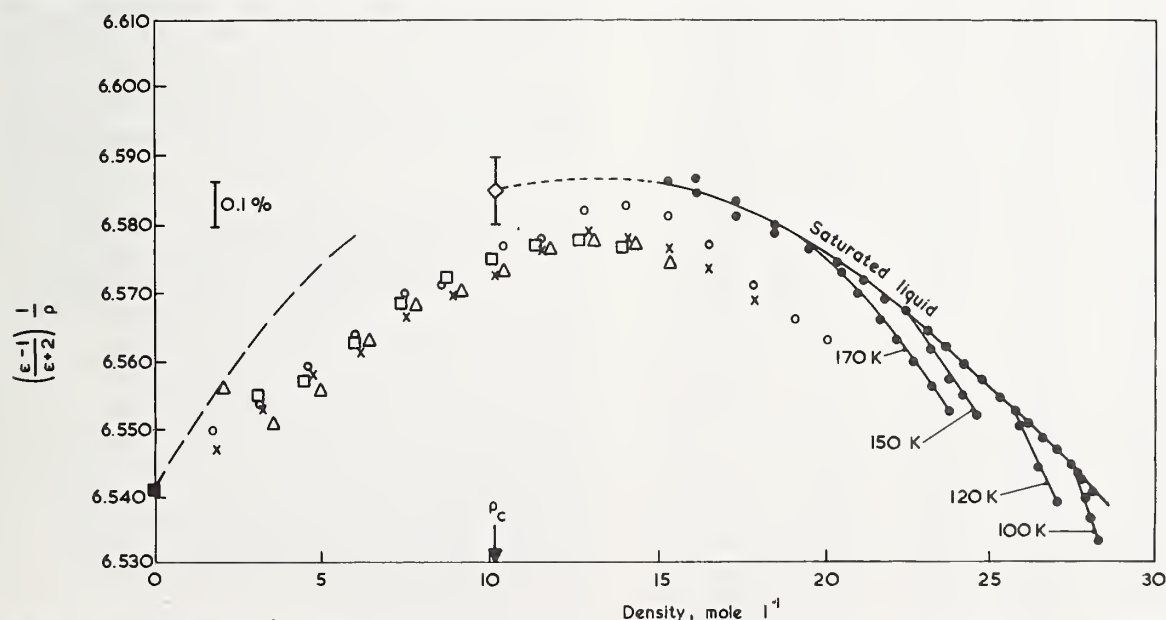


Fig.2 Molar polarizability ( $\text{cm}^3 \text{ mole}^{-1}$ ) as a function of density ( $\text{mole l}^{-1}$ ) for saturated and compressed fluid methane ○ 220 K; X 250 K; Δ 280 K; □ 300 K; ● saturated and compressed liquid as indicated. The broken line and its intercept ■ are from reference 9 (see text).  
 ♦ Extrapolated value of  $\theta$  at critical density

Table 2. Dielectric constant and polarizability of compressed fluid methane

| $T$ ,<br>K | Pressure,<br>bar<br>(1 bar =<br>$10^5 \text{ N m}^{-2}$ ) | $\rho$ ,<br>$\text{mole l}^{-1}$ | $\epsilon$ | $\theta$ ,<br>$\text{cm}^3 \text{ mole}^{-1}$ | $T$ ,<br>K | Pressure,<br>bar<br>(1 bar =<br>$10^5 \text{ N m}^{-2}$ ) | $\rho$ ,<br>$\text{mole l}^{-1}$ | $\epsilon$ | $\theta$ ,<br>$\text{cm}^3 \text{ mole}^{-1}$ |
|------------|-----------------------------------------------------------|----------------------------------|------------|-----------------------------------------------|------------|-----------------------------------------------------------|----------------------------------|------------|-----------------------------------------------|
| 100.000    | 228.079                                                   | 28.314                           | 1.68094    | 6.5336                                        | 280.000    | 45.150                                                    | 2.143                            | 1.04275    | 6.5567                                        |
| 100.000    | 153.203                                                   | 28.031                           | 1.67300    | 6.5366                                        | 300.000    | 330.057                                                   | 13.911                           | 1.30214    | 6.5773                                        |
| 100.000    | 97.110                                                    | 27.801                           | 1.66663    | 6.5396                                        | 300.000    | 280.913                                                   | 12.604                           | 1.27122    | 6.5781                                        |
| 100.000    | 51.839                                                    | 27.598                           | 1.66117    | 6.5436                                        | 300.000    | 242.818                                                   | 11.370                           | 1.24249    | 6.5774                                        |
| 120.000    | 266.417                                                   | 27.022                           | 1.64387    | 6.5390                                        | 300.000    | 209.259                                                   | 10.082                           | 1.21299    | 6.5752                                        |
| 120.000    | 147.997                                                   | 26.448                           | 1.62795    | 6.5443                                        | 300.000    | 179.506                                                   | 8.766                            | 1.18342    | 6.5724                                        |
| 120.000    | 50.442                                                    | 25.884                           | 1.61252    | 6.5506                                        | 300.000    | 151.916                                                   | 7.414                            | 1.15359    | 6.5688                                        |
| 150.000    | 348.259                                                   | 25.286                           | 1.59475    | 6.5431                                        | 300.000    | 124.943                                                   | 6.011                            | 1.12321    | 6.5631                                        |
| 150.000    | 234.488                                                   | 24.553                           | 1.57517    | 6.5522                                        | 300.000    | 98.027                                                    | 4.590                            | 1.09310    | 6.5576                                        |
| 150.000    | 167.521                                                   | 24.046                           | 1.56140    | 6.5555                                        | 300.000    | 71.072                                                    | 3.205                            | 1.06438    | 6.5551                                        |
| 150.000    | 117.544                                                   | 23.608                           | 1.54951    | 6.5576                                        |            |                                                           |                                  |            |                                               |
| 150.000    | 64.940                                                    | 23.053                           | 1.53473    | 6.5622                                        |            |                                                           |                                  |            |                                               |
| 150.000    | 23.946                                                    | 22.492                           | 1.52074    | 6.5759                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 322.417                                                   | 23.642                           | 1.54996    | 6.5527                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 261.170                                                   | 23.138                           | 1.53653    | 6.5567                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 200.661                                                   | 22.555                           | 1.52099    | 6.5603                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 154.135                                                   | 22.019                           | 1.50678    | 6.5632                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 116.695                                                   | 21.501                           | 1.49316    | 6.5662                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 81.608                                                    | 20.903                           | 1.47759    | 6.5701                                        |            |                                                           |                                  |            |                                               |
| 170.000    | 54.927                                                    | 20.328                           | 1.46270    | 6.5735                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 343.100                                                   | 20.000                           | 1.45331    | 6.5634                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 274.601                                                   | 18.982                           | 1.42716    | 6.5664                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 213.396                                                   | 17.725                           | 1.39549    | 6.5713                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 171.259                                                   | 16.473                           | 1.36454    | 6.5772                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 142.848                                                   | 15.249                           | 1.33469    | 6.5819                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 122.996                                                   | 14.014                           | 1.30494    | 6.5838                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 108.846                                                   | 12.760                           | 1.27507    | 6.5820                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 98.454                                                    | 11.494                           | 1.24537    | 6.5782                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 90.162                                                    | 10.192                           | 1.21544    | 6.5737                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 82.842                                                    | 8.853                            | 1.18534    | 6.5720                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 75.722                                                    | 7.512                            | 1.15576    | 6.5703                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 67.738                                                    | 6.133                            | 1.12584    | 6.5644                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 58.009                                                    | 4.728                            | 1.09602    | 6.5595                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 45.581                                                    | 3.301                            | 1.06634    | 6.5541                                        |            |                                                           |                                  |            |                                               |
| 220.000    | 28.747                                                    | 1.842                            | 1.03663    | 6.5500                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 345.558                                                   | 17.729                           | 1.39544    | 6.5692                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 284.251                                                   | 16.512                           | 1.36527    | 6.5735                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 238.340                                                   | 15.295                           | 1.33551    | 6.5764                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 203.208                                                   | 14.059                           | 1.30573    | 6.5783                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 176.512                                                   | 12.831                           | 1.27660    | 6.5790                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 154.248                                                   | 11.523                           | 1.24600    | 6.5770                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 136.108                                                   | 10.211                           | 1.21585    | 6.5736                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 120.569                                                   | 8.906                            | 1.18643    | 6.5698                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 105.714                                                   | 7.550                            | 1.15650    | 6.5668                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 90.896                                                    | 6.181                            | 1.12682    | 6.5618                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 74.891                                                    | 4.780                            | 1.09709    | 6.5580                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 56.522                                                    | 3.343                            | 1.06719    | 6.5534                                        |            |                                                           |                                  |            |                                               |
| 250.000    | 34.727                                                    | 1.884                            | 1.03746    | 6.5472                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 333.164                                                   | 15.299                           | 1.33549    | 6.5743                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 290.178                                                   | 14.249                           | 1.31025    | 6.5775                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 250.396                                                   | 13.053                           | 1.28177    | 6.5777                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 215.396                                                   | 11.749                           | 1.25122    | 6.5767                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 186.296                                                   | 10.430                           | 1.22083    | 6.5735                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 161.737                                                   | 9.130                            | 1.19144    | 6.5704                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 139.635                                                   | 7.827                            | 1.16259    | 6.5688                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 117.974                                                   | 6.474                            | 1.13312    | 6.5634                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 95.475                                                    | 5.057                            | 1.10287    | 6.5561                                        |            |                                                           |                                  |            |                                               |
| 280.000    | 71.641                                                    | 3.616                            | 1.07278    | 6.5511                                        |            |                                                           |                                  |            |                                               |

(see Appendix). The uncertainty in the calculated polarizabilities is estimated to be better than  $\pm 0.15\%$  at low densities where  $\epsilon - 1$  is small, decreasing to about  $\pm 0.1\%$  at higher densities and is limited by the accuracy of the densities, estimated by Goodwin and Prydz<sup>1</sup> as  $\pm 0.1\%$ . The overall precision is better as reflected by the scatter of the data.

Our experimental apparatus and procedures were designed for making measurements over a wide pressure and density range and are not particularly suitable for making high precision measurements at low density where  $\epsilon - 1$  becomes very small. As a result, attempts to extract dielectric virial coefficients from these data must be approached with some caution. Bose et al<sup>10</sup> have recently published the results of high precision measurements of the dielectric constant of methane at pressures below about 100 bar. They use an expansion technique to obtain relative densities. The polarizability for their 279.8 K isotherm calculated using their virial coefficients is shown in Fig. 2 for comparison with our 280 K data. The value of  $A_\epsilon$ , the zero density intercept, is the most directly and accurately determined quantity in their experiments. They obtained a slightly temperature dependent value for  $A_\epsilon$  but select  $A_\epsilon = 6.541 \text{ cm}^3 \text{ mole}^{-1}$  as a best value which is consistent with our data. Their value for  $B_\epsilon$  however appears to be somewhat large when compared to our higher density data.

Attempts to simply fit the polarizability data to (2) were unsatisfactory. For those isotherms which exhibit a maximum in the polarizability however, an additional constraint can be imposed, that is,  $C_\epsilon = -B_\epsilon/2\rho_{\text{max}}$  where  $\rho_{\text{max}}$  is the density at the maximum in the polarizability. Using the temperature dependent values of  $A_\epsilon$  from reference 9, a large number of one parameter ( $B_\epsilon$ ) fits with  $\rho_{\text{max}}$  constrained to the limits  $12.0 \text{ mole l}^{-1} \leq \rho_{\text{max}} \leq 16.0 \text{ mole l}^{-1}$  resulted in a best fit with the parameters in Table 3. These curves are shown together with the experimental data in Fig. 3. Note that the curves do not fit the data well at low densities. The vertical bars, however, indicate the variation in the polarizability which could result from  $\pm 0.1\%$  variation in density. The slight oscillatory behaviour of the isothermal data is believed to be the result of the polynomials used to represent the  $P\rho T$  data<sup>1</sup> (see Appendix).

The scatter in our low density data for the various isotherms does not permit us to resolve the temperature

dependence of  $B_E$  although the data do suggest that it is small. This is to be expected since the  $1/T$  dependence of  $B_E$  arises from dipole moments induced in one molecule by multipole moments in the other. The first non-vanishing multipole is the octopole in methane because of its tetrahedral symmetry and octupole effects should be small.

## APPENDIX

We discuss briefly the method of obtaining densities from the  $P\rho T$  data of Goodwin and Prydz.<sup>1</sup> They have measured the density of methane from the triple point to 300 K at pressures up to about 340 bar. They chose to represent their data by a unique, non-analytic equation of state capable of reproducing the experimental data to reasonable accuracy over the complete region of the state surface investigated. Because of the importance of density in the calculation of the polarizability from dielectric constant measurements, severe demands are made on the representation of the  $P\rho T$  data and it was found that the equation of state was not adequate for our analysis. The somewhat sparse experimental  $P\rho T$  data along isotherms were therefore fitted to polynomials of the form

$$P = \rho R T + \sum_n A_n \rho^n$$

and an iterative procedure was then used to calculate the density from the measured temperature and pressure.

Experimental saturated liquid densities were represented by an equation, derived by Goodwin,<sup>1</sup> of the form

$$\frac{(\rho - \rho_c)}{(\rho_t - \rho_c)} = \omega^a \exp [b(1 - \omega^{2/3}) + c(1 - \omega^{4/3}) + d(1 - \omega^2)]$$

where  $\omega = (T_c - T)/(T_c - T_t)$ ,  $a = 0.36$  consistent with scaling theory, and the subscripts c and t refer to the values at the critical and triple points respectively. This equation reproduced the experimental saturated liquid densities to within the accuracy of the data.

The authors wish to express their appreciation to Dr J. F. Ely and Dr J. D. Olson for helpful discussions and assistance with the calculations.

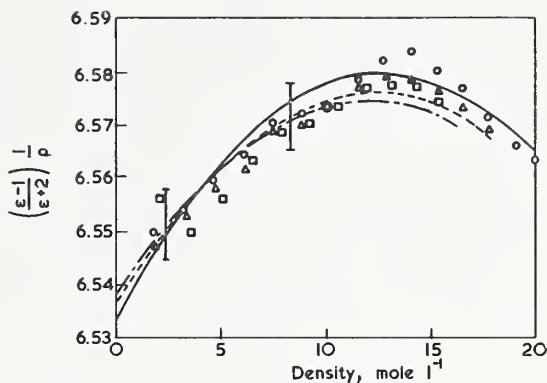


Fig. 3 Fit of the molar polarizability data ( $\text{cm}^3 \text{mole}^{-1}$ ) as a function of density ( $\text{mole l}^{-1}$ ) for  $\circ$  220 K;  $\triangle$  250 K;  $\square$  280 K; — 220 K; --- 250 K; - - - 280 K (see text). The vertical bars indicate the possible effect of the  $\pm 0.1\%$  uncertainty in the densities of reference 1.

Table 3. Dielectric virial coefficients of methane

| $T$ ,<br>K | $A_E$ ,<br>$\text{cm}^3 \text{mole}^{-1}$ | $B_E$ ,<br>$(\text{cm}^3 \text{mole}^{-1})^2$ | $C_E$ ,<br>$(\text{cm}^3 \text{mole}^{-1})^3$ | $\rho_{\text{max}}$ ,<br>$\text{mole l}^{-1}$ |
|------------|-------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 220        | 6.534                                     | 7.10                                          | -278.4                                        | 12.75                                         |
| 250        | 6.536                                     | 6.53                                          | -266.5                                        | 12.25                                         |
| 280        | 6.538                                     | 6.07                                          | -252.7                                        | 12.00                                         |

\*Values of  $A_E$  calculated from reference 9

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## APPENDIX F



*Measurements of the velocity of sound in saturated and compressed fluid methane are reported. Measurements were made on the saturated liquid from 91 K to 186 K and on the compressed fluid along selected isotherms from 100 K to 300 K at pressures to about 35 MN m<sup>-2</sup>. Data were combined with newly available PpT data to obtain the isentropic compressibility and the ratio of the specific heats. Measurements along the higher temperature isotherm were limited to densities greater than about 10 mole l<sup>-1</sup> at 300 K increasing to about 14 mole l<sup>-1</sup> at 210 K due to the large low pressure sound attenuation in methane.*

## Velocity of sound in dense fluid methane

G. C. Straty

The increased handling, storage, and transportation of fuel gases in the liquid state has created a need for wide range thermodynamic and transport properties data on these fluids in engineering and development applications. The properties of methane are particularly important since it is the principal constituent of liquefied natural gas (LNG). Sound velocity measurements, when combined with newly available pressure, density, temperature (*PpT*) data<sup>1,2</sup> offer a convenient and more accurate method of obtaining certain thermodynamic quantities which cannot easily be determined by other means, as well as providing a sensitive check on the *PpT* surface and its derivatives.

The well-known equations

$$W^2 = (\rho\kappa_S)^{-1} = \gamma \left( \frac{\partial P}{\partial \rho} \right)_T$$

relate the sound velocity *W* to the density  $\rho$ , the isentropic compressibility  $\kappa_S$ , and the ratio of specific heats,  $\gamma$ . This relation has been used together with *PpT* data<sup>1,2</sup> to determine  $\kappa_S$  and  $\gamma$  from the measured sound velocities for saturated and compressed fluid methane.

Measurements of the sound velocity for saturated liquid methane have been made from near the triple point to 186 K and on compressed fluid methane along several isotherms from 100 K to 300 K at pressures to about 35 MN m<sup>-2</sup>. Measurements, in our apparatus, on the compressed fluid were limited however to minimum pressures corresponding to densities ranging from about 10 mole l<sup>-1</sup> at 300 K to about 14 mole l<sup>-1</sup> at 210 K because of the large sound attenuation in low pressure gaseous methane.

### Experimental

The pulse echo technique was used for the sound velocity measurements. The apparatus was identical to that used previously in this laboratory for measurements on hydrogen,<sup>3</sup> oxygen,<sup>4</sup> and fluorine<sup>5</sup> and has been described in detail. Uncertainty in the measured velocities is estimated at about 0.05% at the higher densities increasing

somewhat in the regions of high attenuation. Measurements were made at frequencies of 1 MHz and 10 MHz with no observable dispersion. Temperatures were measured using a platinum resistance thermometer calibrated by the National Bureau of Standards on the IPTS 1968. Uncertainty in temperature is estimated at 0.005 K at the lower temperatures increasing to 0.030 K at 300 K.<sup>6</sup> Pressures were measured by referencing to oil pressures derived from an oil dead weight gauge, accurate to within 0.01%, through differential pressure transducers.<sup>7</sup> The methane used was a commercially available, ultra high purity (99.97%) grade.

### Results

The measured sound velocities for the saturated liquid are tabulated along with the density and the calculated compressibility and specific heat ratio in Table 1. Also shown in Table 1, for comparison, are the sound velocities interpolated from the data of Blagoi et al.<sup>8</sup> and Van Dael et al.<sup>9</sup> and the sound velocities calculated by Goodwin<sup>2</sup> directly from *PpT* and specific heat data.

Sound velocities for the compressed fluid along several isotherms and for the saturated liquid are shown as a function of density in Fig. 1 and are tabulated along with the measured pressures and temperatures and the derived values of compressibility and specific heat ratio in Table 2. Van Itterbeek et al.<sup>10</sup> have also made measurements on the compressed liquid at 190 K and below but their data are not directly comparable with the present data without multiple interpolations. Their compressed liquid data however were obtained on the same apparatus as the saturated liquid data of Van Dael et al.<sup>8</sup> and our agreement with these saturated liquid values is indicative of the overall agreement. No ultrasonic data are available for comparison at temperatures above 190 K.

Densities for the saturated liquid were obtained from the measured temperatures and a correlation for the saturated liquid densities due to Goodwin.<sup>2</sup> Densities for the compressed fluid and the derivatives necessary for the calculations were obtained from the measured temperatures and pressures and an equation of state for methane also due to Goodwin.<sup>2</sup>

The uncertainty in the derived isentropic compressibilities is estimated at about  $\pm 0.2\%$  due to the combined uncertainty

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Table 1 Velocity of sound  $W$  and derived values of the isentropic compressibility  $\kappa_s$  and ratio  $\gamma$  of the heat capacities in saturated liquid methane at temperature  $T$  and density  $\rho$

| $T, K$ | $W, m s^{-1}$ |             |             |                  | $\rho, mole l^{-1}$ | $\kappa_s, (G N m^{-2})^{-1}$ | $\gamma$ |
|--------|---------------|-------------|-------------|------------------|---------------------|-------------------------------|----------|
|        | Expt          | Reference 9 | Reference 8 | Calc Reference 2 |                     |                               |          |
| 91.0   | 1538.1        |             | 1530.2      |                  | 28.121              | 0.9369                        | 1.525    |
| 92.0   | 1528.7        |             | 1522.0      | 1564             | 28.038              | 0.9514                        | 1.530    |
| 96.0   | 1490.6        | 1491.5      | 1487.3      | 1523             | 27.703              | 1.013                         | 1.551    |
| 100.0  | 1452.2        | 1451.4      | 1442.8      | 1480             | 27.364              | 1.080                         | 1.575    |
| 104.0  | 1413.4        | 1413.2      | 1401.5      | 1437             | 27.020              | 1.155                         | 1.601    |
| 108.0  | 1373.8        | 1374.6      | 1364.6      | 1393             | 26.669              | 1.238                         | 1.629    |
| 112.0  | 1334.1        | 1334.7      | 1352.2      | 1351             | 26.310              | 1.331                         | 1.660    |
| 116.0  | 1294.0        | 1294.1      | 1208.7      | 1308             | 25.943              | 1.435                         | 1.693    |
| 120.0  | 1252.9        | 1253.6      | 1245.3      | 1266             | 25.567              | 1.553                         | 1.726    |
| 124.0  | 1211.3        | 1212.6      | 1207.6      | 1224             | 25.181              | 1.687                         | 1.763    |
| 128.0  | 1169.1        | 1170.0      | 1165.2      | 1181             | 24.783              | 1.840                         | 1.801    |
| 132.0  | 1126.0        | 1227.0      | 1120.4      | 1138             | 24.372              | 2.017                         | 1.842    |
| 136.0  | 1082.2        | 1083.0      | 1079.2      | 1093             | 23.947              | 2.222                         | 1.886    |
| 140.0  | 1037.4        | 1038.0      | 1034.7      | 1047             | 23.507              | 2.464                         | 1.933    |
| 144.0  | 991.7         | 992.4       | 987.2       | 999              | 23.050              | 2.750                         | 1.986    |
| 148.0  | 944.8         | 945.3       | 946.5       | 951              | 22.572              | 3.094                         | 2.045    |
| 150.0  | 921.0         | 921.4       | 921.4       | 927              | 22.324              | 3.292                         | 2.079    |
| 152.0  | 896.6         | 897.2       | 896.3       | 902              | 22.071              | 3.513                         | 2.114    |
| 156.0  | 846.9         | 847.6       | 850.2       | 852              | 21.524              | 4.034                         | 2.195    |
| 160.0  | 795.5         | 796.0       | 796.4       | 802              | 20.981              | 4.695                         | 2.295    |
| 164.0  | 742.2         | 742.5       | 746.0       | 749              | 20.379              | 5.552                         | 2.423    |
| 168.0  | 686.3         | 686.7       | 684.6       | 695              | 19.724              | 6.709                         | 2.590    |
| 170.0  | 657.5         | 657.5       | 657.5       | 667              | 19.373              | 7.444                         | 2.698    |
| 172.0  | 627.5         | 628.2       | 632.2       | 637              | 19.001              | 8.331                         | 2.824    |
| 176.0  | 564.1         | 564.8       | 568.0       | 570              | 18.183              | 10.77                         | 3.168    |
| 178.0  | 530.5         | 530.8       |             | 536              | 17.725              | 12.50                         | 3.413    |
| 180.0  | 495.0         | 495.5       |             | 500              | 17.222              | 14.77                         | 3.736    |
| 182.0  | 457.7         | 458.0       |             | 462              | 16.662              | 17.86                         | 4.195    |
| 184.0  | 417.2         | 415.8       |             | 421              | 16.022              | 22.35                         | 4.882    |
| 186.0  | 370.9         | 371.7       |             | 377              | 15.263              | 29.68                         | 6.012    |

Columns 3, 4 and 5 give values of  $W$  from references 9 and 8 and those calculated from  $P\rho T$  data in reference 2

in the experimental densities of  $\pm 0.1\%$ <sup>1,2</sup> and the equation of state correlation.<sup>2</sup> The uncertainty in  $\gamma$  is difficult to assess, depending almost entirely on the accuracy of the derivative  $(\partial P/\partial \rho)_T$  used to obtain  $\gamma$  from the sound velocity. Goodwin,<sup>2</sup> however, has shown that his equation of state can be used successfully for the calculation of wide range self-consistent thermodynamic functions involving extensive use of both first and second derivatives of the  $P\rho T$  surface, which adds confidence to the accuracy of values of  $(\partial P/\partial \rho)_T$  used here. Comparison of the measured sound velocities with those calculated from the equation of state suggests<sup>11</sup> that the uncertainty in  $\gamma$  is probably less than 1.0% at the higher temperatures increasing somewhat for the low temperature, high density liquid where  $(\partial P/\partial \rho)_T$  is very large and most difficult to determine accurately from  $P\rho T$  data.

This work was sponsored by the American Gas Association Inc.

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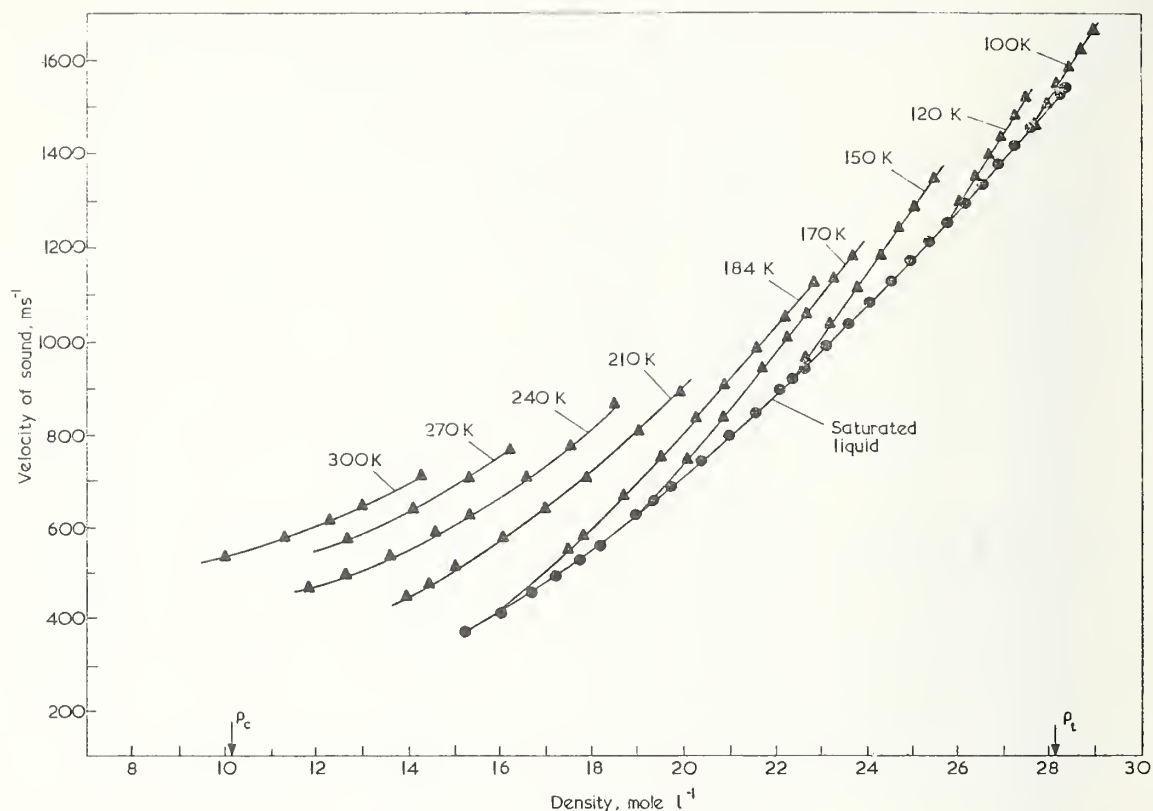


Fig.1 Velocity of sound plotted against density for saturated and compressed fluid methane

Table 2 Velocity of sound  $W$  and derived values of the isentropic compressibility  $\kappa_s$  and ratio  $\gamma$  of heat capacities in compressed fluid methane at temperature  $T$  and density  $\rho$

| $P$ ,<br>M N m <sup>-2</sup> | $W$ , m s <sup>-1</sup> |                | $\rho$ , mole l <sup>-1</sup> | $\kappa_s$ ,<br>(G N m <sup>-2</sup> ) <sup>-1</sup> | $\gamma$ |
|------------------------------|-------------------------|----------------|-------------------------------|------------------------------------------------------|----------|
|                              |                         | Calc           |                               |                                                      |          |
|                              | Expt                    | Reference<br>2 |                               |                                                      |          |
| $T = 100.0$ K                |                         |                |                               |                                                      |          |
| 33.385                       | 1672.6                  | 1610.3         | 28.692                        | 0.7766                                               | 1.576    |
| 26.077                       | 1630.7                  | 1589.5         | 28.430                        | 0.8245                                               | 1.566    |
| 19.123                       | 1588.1                  | 1566.0         | 28.169                        | 0.8774                                               | 1.561    |
| 13.088                       | 1548.5                  | 1542.4         | 27.930                        | 0.9307                                               | 1.561    |
| 7.244                        | 1507.4                  | 1516.5         | 27.686                        | 0.9908                                               | 1.565    |
| 1.661                        | 1465.1                  | 1488.9         | 27.439                        | 1.058                                                | 1.572    |
| $T = 120.0$ K                |                         |                |                               |                                                      |          |
| 31.161                       | 1517.2                  | 1475.3         | 27.225                        | 0.9947                                               | 1.611    |
| 26.233                       | 1482.8                  | 1449.5         | 27.004                        | 1.050                                                | 1.620    |
| 19.980                       | 1436.0                  | 1413.4         | 26.707                        | 1.132                                                | 1.635    |
| 15.149                       | 1397.0                  | 1382.7         | 26.460                        | 1.207                                                | 1.651    |
| 9.258                        | 1345.2                  | 1341.3         | 26.136                        | 1.318                                                | 1.675    |
| 4.367                        | 1290.5                  | 1302.8         | 25.841                        | 1.448                                                | 1.681    |
| $T = 150.0$ K                |                         |                |                               |                                                      |          |
| 34.530                       | 1339.6                  | 1303.6         | 25.275                        | 1.374                                                | 1.700    |
| 28.845                       | 1290.0                  | 1260.0         | 24.923                        | 1.503                                                | 1.727    |
| 23.669                       | 1240.3                  | 1216.1         | 24.572                        | 1.649                                                | 1.758    |
| 18.433                       | 1184.6                  | 1166.4         | 24.178                        | 1.837                                                | 1.797    |

| $P$ ,<br>M N m <sup>-2</sup> | $W$ , m s <sup>-1</sup> |                        | $\rho$ , mole l <sup>-1</sup> | $K_s$ ,<br>(G N m <sup>-2</sup> ) <sup>-1</sup> | $\gamma$ |
|------------------------------|-------------------------|------------------------|-------------------------------|-------------------------------------------------|----------|
|                              | Expt                    | Calc<br>Reference<br>2 |                               |                                                 |          |
| 12.667                       | 1114.5                  | 1103.3                 | 23.682                        | 2.119                                           | 1.855    |
| 7.263                        | 1036.6                  | 1032.5                 | 23.132                        | 2.508                                           | 1.931    |
| 3.020                        | 962.1                   | 964.4                  | 22.609                        | 2.979                                           | 2.021    |
| $T = 170.0$ K                |                         |                        |                               |                                                 |          |
| 31.457                       | 1183.8                  | 1169.0                 | 23.584                        | 1.886                                           | 1.778    |
| 26.994                       | 1135.5                  | 1124.7                 | 23.213                        | 2.082                                           | 1.813    |
| 20.773                       | 1059.2                  | 1053.8                 | 22.619                        | 2.456                                           | 1.877    |
| 17.538                       | 1013.9                  | 1011.2                 | 22.263                        | 2.724                                           | 1.922    |
| 13.012                       | 940.7                   | 941.9                  | 21.684                        | 3.249                                           | 2.009    |
| 7.774                        | 833.5                   | 838.6                  | 20.819                        | 4.309                                           | 2.183    |
| 4.528                        | 742.9                   | 750.5                  | 20.078                        | 5.624                                           | 2.397    |
| $T = 184.0$ K                |                         |                        |                               |                                                 |          |
| 34.254                       | 1129.0                  | 1119.8                 | 22.751                        | 2.150                                           | 1.794    |
| 27.883                       | 1055.1                  | 1050.5                 | 22.145                        | 2.528                                           | 1.850    |
| 22.511                       | 982.8                   | 981.6                  | 21.538                        | 2.996                                           | 1.919    |
| 17.863                       | 909.0                   | 910.3                  | 20.903                        | 3.609                                           | 2.007    |
| 13.839                       | 831.9                   | 834.9                  | 20.221                        | 4.454                                           | 2.126    |
| 10.436                       | 751.2                   | 754.2                  | 19.475                        | 5.672                                           | 2.301    |
| 7.722                        | 666.6                   | 669.4                  | 18.661                        | 7.517                                           | 2.561    |
| 5.770                        | 579.9                   | 584.5                  | 17.809                        | 10.41                                           | 2.934    |
| 5.301                        | 552.8                   | 558.2                  | 17.535                        | 11.63                                           | 3.091    |
| $T = 210.0$ K                |                         |                        |                               |                                                 |          |
| 34.074                       | 987.0                   | 988.0                  | 20.741                        | 3.085                                           | 1.843    |
| 27.598                       | 898.0                   | 901.2                  | 19.885                        | 3.887                                           | 1.929    |
| 22.264                       | 809.8                   | 813.7                  | 18.981                        | 5.007                                           | 2.045    |
| 17.486                       | 711.5                   | 714.8                  | 17.885                        | 6.884                                           | 2.228    |
| 14.832                       | 643.9                   | 646.2                  | 17.053                        | 8.817                                           | 2.405    |
| 12.703                       | 577.5                   | 579.5                  | 16.159                        | 11.56                                           | 2.635    |
| 10.944                       | 511.5                   | 512.1                  | 15.124                        | 15.76                                           | 2.988    |
| 10.173                       | 477.0                   | 477.4                  | 14.512                        | 18.88                                           | 3.239    |
| 9.646                        | 451.2                   | 451.3                  | 14.001                        | 21.86                                           | 3.481    |
| $T = 240.0$ K                |                         |                        |                               |                                                 |          |
| 34.638                       | 863.5                   | 870.2                  | 18.505                        | 4.517                                           | 1.871    |
| 29.111                       | 782.7                   | 789.0                  | 17.531                        | 5.803                                           | 1.964    |
| 24.656                       | 707.0                   | 712.4                  | 16.520                        | 7.549                                           | 2.076    |
| 20.885                       | 632.6                   | 636.8                  | 15.395                        | 10.12                                           | 2.221    |
| 18.890                       | 588.8                   | 591.9                  | 14.637                        | 12.28                                           | 2.330    |
| 16.841                       | 540.2                   | 541.7                  | 13.673                        | 15.62                                           | 2.478    |
| 15.186                       | 498.4                   | 498.8                  | 12.697                        | 19.77                                           | 2.617    |
| 14.071                       | 469.8                   | 470.0                  | 11.907                        | 23.72                                           | 2.698    |
| $T = 270.0$ K                |                         |                        |                               |                                                 |          |
| 34.769                       | 771.5                   | 775.8                  | 16.311                        | 6.420                                           | 1.867    |
| 30.486                       | 711.2                   | 714.6                  | 15.387                        | 8.010                                           | 1.935    |
| 25.972                       | 641.6                   | 643.6                  | 14.167                        | 10.69                                           | 2.029    |
| 21.837                       | 572.8                   | 573.3                  | 12.708                        | 14.95                                           | 2.131    |
| $T = 300.0$ K                |                         |                        |                               |                                                 |          |
| 34.838                       | 713.9                   | 713.7                  | 14.331                        | 8.534                                           | 1.818    |
| 29.732                       | 649.5                   | 648.5                  | 13.065                        | 11.31                                           | 1.873    |
| 27.295                       | 618.0                   | 616.7                  | 12.352                        | 13.21                                           | 1.896    |
| 24.427                       | 580.4                   | 580.1                  | 11.404                        | 16.23                                           | 1.904    |
| 20.983                       | 537.3                   | 537.9                  | 10.094                        | 21.39                                           | 1.896    |

Column 3 gives the value of  $W$  calculated from  $P\rho T$  data



## APPENDIX G

# The Specific Heats, $C_p$ , and $C_v$ , of Compressed and Liquefied Methane\*

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(January 30, 1974)

The specific heats,  $C_p$ , of saturated liquid methane have been measured at 66 temperatures in the temperature range 95–187 K. The specific heats at constant volume,  $C_v$ , have been measured at 20 densities ranging from 0.8 to 2.8 times the critical density, at temperatures between 91 and 300 K, and at pressures to 330 bar (at 280 *PIT* states in all). The uncertainty of most of the measurements is estimated to be less than 0.5 percent, except near the critical point. These measurements were performed primarily to provide input data for accurate thermodynamic properties data calculations for liquid methane. They are believed to be the most comprehensive specific heat measurements available for pure compressed gaseous and liquid methane.

Key words: Constant volume; heat capacity; liquid; saturated liquid; specific heat; methane.

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\*This work was carried out at the National Bureau of Standards under the sponsorship of The American Gas Association.

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## 1. Introduction

For the calculation of fluid thermodynamic properties such as internal energy, enthalpy, entropy, and velocity of sound, at temperatures less than the critical point, one needs either the latent heat of vaporization or specific heat along a path traversing the temperatures of interest. Heat capacity measurements are much easier than latent heat measurements and the specific heat measurements are not restricted to the liquid-vapor curve but can be made covering temperatures and densities in the single phase fluid region as well.

For methane, specific heat of the saturated liquid,  $C_\sigma$ , was measured from 95 to 187 K, and specific heat at constant volume,  $C_V$ , was measured on 20 isochlores with densities ranging from 8 mol/l to 28 mol/l, temperatures from 90 to 300 K, and pressures to 330 bar [1].<sup>1</sup>

## 2. Apparatus

The specific heats were obtained using a constant volume adiabatic calorimeter, as described previously by Goodwin [2]. Basically, it consists of a thin spherical stainless-steel sample holder bearing a heater and platinum resistance thermometer and enclosed in an adiabatic shield. The calorimeter and cryostat are shown in figure 1. The refrigerant was liquid nitrogen.

The versatility of this instrument is demonstrated in that it has been used with very minor modifications for the  $C_V$  and  $C_\sigma$  measurements of hydrogen [3, 4], oxygen [5, 6], fluorine [7, 8], and in this work on methane. These measurements cover temperatures from 14 to 300 K and pressures to 330 bar.

The thermometer was calibrated by the NBS Temperature Section. Temperatures are on the IPTS-68 scale. The temperature of the adiabatic shield and guard ring are controlled to the sample temperature with difference thermocouples and automatic power regulation. Heat exchange to the sample holder is considered negligible.

The sample used was 99.99 percent methane. Impurities as analyzed by the supplier in ppm were  $\text{CO}_2 < 10$ ;  $\text{O}_2$ , 4;  $\text{N}_2$ , 12. A molecular sieve in an ice bath served to ensure removal of water vapor present in the sample.

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

### 3. Procedure

In essence, the specific heat  $C_V$  is calculated from the measured parameters as follows. The total heat capacity is determined as the ratio of the heat input  $\Delta Q$  to the temperature increase  $\Delta T$  brought about by applying a very stable power source to a resistor attached to the calorimeter sample holder, for an elapsed time  $\Delta t$ . The heat capacity of the empty sample holder  $C_0$  is then subtracted off. It, of course, was previously measured in exactly the same way except with the sample space pumped to a vacuum. The difference of these two quantities is the heat capacity of the methane sample. The specific heat is obtained by dividing the heat capacity by the amount of methane,  $N$ .

Actually, several corrections are made to the above. Since the sample holder is a thin stainless steel sphere ( $\sim 0.16$  mm wall thickness and 5 cm diam), it stretches as the pressure increases. This allows work to be done by the methane due to the increase of the sample volume. This correction [4, 5, 6], developed by Walker [9], ranges from 0.5 to 5 percent of the resulting  $C_V$  value. However, it can be made accurately.

Of the three variables, pressure, temperature, and density, only temperature is measured during the measurement of an isochore. The pressure and temperature are measured at filling and the density calculated from the  $PVT$  surface [10]. The amount of methane,  $N$ , is calculated from the volume  $V(T, P)$  as previously determined [3, 5]. The density for each  $C_V$  measurement is calculated from the filling density after correcting for sample holder expansion and the amount compressed into the filling capillary [6].

In the case of the  $C_p$  measurement, the two phase heat capacity (liquid and gas) is first determined as the difference of the total heat capacity ( $DQ/DT$ , column 6 of table 1) and the empty heat capacity ( $C_0$ , column 7) and the result divided by the total amount of sample ( $C_2$ , column 8). Then the effects of the latent heat of vaporization and heat absorbed by the vapor are subtracted [3, 5, 7] to give  $C_p$  (column 10). This type of correction is derived by Hoge [11].

The temperature increment, resulting from a constant power input over a time  $\Delta t$ , is evaluated at the middle of the heating interval by extrapolating the temperature drift rates evaluated just before heating and after an equilibrating time has elapsed (about 20 min). Care was taken to reduce the effects of noise on drift rate by taking many (10 to 20) measurements of time and temperature.

TABLE 1. Specific heat of saturated liquid methane,  $C_p$  or  $C_{s,l}$ ; specific heat at constant volume of saturated liquid calculated,  $C_v$ ; specific heat of the two phase (liquid-vapor) system,  $C_2$ ; heat capacity of the calorimeter (empty)  $C_0$ , and heat capacity of the calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $\Delta T$

| ID   | Temp K  | Press bar | Dens mol/l | Delt K | $DQ/DT$ J/K | $C_0$ J/K | $C_2$ J/mol · K | $C_v$ J/mol · K | $C_{sat}$ J/mol · K |
|------|---------|-----------|------------|--------|-------------|-----------|-----------------|-----------------|---------------------|
| 201  | 95.402  | 0.209     | 27.755     | 3.657  | 133.482     | 46.671    | 54.418          | 34.274          | 54.240              |
| 401  | 95.846  | .219      | 27.718     | 5.799  | 139.159     | 46.881    | 54.252          | 34.103          | 54.131              |
| 202  | 99.021  | .311      | 27.450     | 3.574  | 135.870     | 48.348    | 54.864          | 34.169          | 54.647              |
| 302  | 101.651 | .409      | 27.224     | 6.638  | 141.300     | 49.520    | 55.058          | 34.016          | 54.877              |
| 402  | 101.961 | .422      | 27.198     | 6.420  | 143.111     | 49.656    | 54.943          | 33.883          | 54.790              |
| 203  | 102.574 | .448      | 27.145     | 3.524  | 137.905     | 49.923    | 55.152          | 33.898          | 54.896              |
| 204  | 106.891 | .673      | 26.767     | 5.110  | 140.924     | 51.750    | 55.899          | 33.941          | 55.602              |
| 303  | 108.219 | .758      | 26.649     | 6.495  | 145.302     | 52.293    | 55.794          | 33.710          | 55.583              |
| 403  | 108.800 | .797      | 26.597     | 7.236  | 146.902     | 52.528    | 55.483          | 33.349          | 55.315              |
| 205  | 112.604 | 1.097     | 26.254     | 6.273  | 144.013     | 54.022    | 56.410          | 33.478          | 56.075              |
| 304  | 115.165 | 1.343     | 26.019     | 7.386  | 149.404     | 54.988    | 56.638          | 33.391          | 56.434              |
| 206  | 119.117 | 1.802     | 25.649     | 6.702  | 147.576     | 56.412    | 57.144          | 33.041          | 56.310              |
| 305  | 122.474 | 2.278     | 25.327     | 7.194  | 153.257     | 57.561    | 57.404          | 32.862          | 57.287              |
| 405  | 123.367 | 2.419     | 25.240     | 7.498  | 154.829     | 57.858    | 57.008          | 32.389          | 56.996              |
| 207  | 125.766 | 2.830     | 25.005     | 6.568  | 151.006     | 58.636    | 57.899          | 32.534          | 57.645              |
| 406  | 130.765 | 3.852     | 24.500     | 7.297  | 158.819     | 60.171    | 57.992          | 32.000          | 58.245              |
| 208  | 132.274 | 4.209     | 24.343     | 6.430  | 154.477     | 60.612    | 58.834          | 32.162          | 58.774              |
| 1001 | 132.751 | 4.326     | 24.293     | 5.117  | 122.552     | 60.750    | 62.894          | 32.148          | 58.879              |
| 902  | 135.455 | 5.038     | 24.007     | 4.538  | 137.072     | 61.512    | 60.813          | 31.499          | 58.930              |
| 1002 | 137.805 | 5.723     | 23.752     | 4.973  | 125.195     | 62.151    | 64.157          | 31.650          | 59.729              |
| 903  | 139.970 | 6.412     | 23.513     | 4.476  | 139.223     | 62.720    | 61.570          | 30.986          | 59.698              |
| 801  | 144.305 | 7.971     | 23.017     | 4.019  | 141.250     | 63.808    | 62.323          | 30.460          | 60.560              |
| 904  | 144.401 | 8.009     | 23.005     | 4.386  | 141.728     | 63.831    | 62.689          | 30.797          | 60.929              |
| 802  | 148.500 | 9.725     | 22.514     | 4.371  | 143.789     | 64.800    | 63.565          | 30.407          | 62.033              |
| 905  | 148.881 | 9.896     | 22.467     | 4.316  | 143.807     | 64.888    | 63.509          | 30.230          | 62.005              |
| 1003 | 150.824 | 10.807    | 22.224     | 4.332  | 133.134     | 65.326    | 68.994          | 31.449          | 64.014              |
| 803  | 152.809 | 11.798    | 21.969     | 4.247  | 146.566     | 65.763    | 65.022          | 30.468          | 63.898              |
| 906  | 153.157 | 11.978    | 21.924     | 4.229  | 146.775     | 65.838    | 65.129          | 30.459          | 64.048              |
| 1004 | 155.542 | 13.267    | 21.606     | 4.941  | 135.238     | 66.345    | 70.092          | 30.518          | 65.246              |
| 804  | 157.043 | 14.128    | 21.401     | 4.180  | 148.588     | 66.657    | 65.926          | 29.932          | 65.435              |
| 907  | 157.355 | 14.312    | 21.358     | 4.167  | 148.747     | 66.721    | 66.001          | 29.899          | 65.569              |
| 1005 | 159.127 | 15.388    | 21.107     | 4.035  | 137.307     | 67.080    | 71.446          | 30.244          | 66.905              |
| 805  | 161.181 | 16.707    | 20.808     | 4.095  | 151.123     | 67.486    | 67.294          | 29.823          | 67.733              |
| 908  | 161.483 | 16.908    | 20.763     | 4.088  | 151.284     | 67.545    | 67.375          | 29.793          | 67.898              |
| 1006 | 163.136 | 18.036    | 20.512     | 3.982  | 138.917     | 67.864    | 72.280          | 29.161          | 68.379              |
| 1402 | 163.782 | 18.492    | 20.412     | 5.441  | 153.354     | 67.987    | 68.702          | 30.257          | 69.936              |
| 806  | 165.249 | 19.556    | 20.179     | 4.036  | 153.713     | 68.263    | 68.749          | 29.716          | 70.534              |
| 1407 | 165.128 | 19.467    | 20.199     | 5.131  | 154.144     | 68.240    | 69.132          | 30.171          | 70.865              |
| 909  | 165.548 | 19.779    | 20.131     | 4.043  | 153.880     | 68.318    | 68.838          | 29.719          | 70.745              |
| 1007 | 166.549 | 20.536    | 19.967     | 2.738  | 141.994     | 68.503    | 74.756          | 29.907          | 71.756              |
| 807  | 169.253 | 22.687    | 19.505     | 3.963  | 156.273     | 68.991    | 70.216          | 29.609          | 73.960              |
| 910  | 169.565 | 22.945    | 19.450     | 3.949  | 156.656     | 69.047    | 70.480          | 29.743          | 74.411              |
| 1220 | 170.157 | 23.440    | 19.344     | 7.335  | 138.896     | 69.151    | 79.614          | 29.404          | 74.696              |
| 1008 | 170.197 | 23.474    | 19.336     | 4.297  | 144.726     | 69.159    | 76.862          | 30.033          | 75.369              |
| 1408 | 170.251 | 23.520    | 19.327     | 5.020  | 157.666     | 69.168    | 71.213          | 30.181          | 75.575              |
| 1403 | 171.097 | 24.243    | 19.172     | 5.271  | 158.018     | 69.316    | 71.376          | 29.980          | 76.320              |
| 808  | 173.180 | 26.094    | 18.773     | 3.890  | 159.054     | 69.675    | 71.898          | 29.577          | 78.540              |
| 911  | 173.480 | 26.369    | 18.714     | 3.873  | 159.572     | 69.727    | 72.273          | 29.813          | 79.194              |
| 701  | 173.505 | 26.392    | 18.709     | 5.002  | 141.928     | 69.731    | 81.284          | 29.262          | 78.678              |
| 1216 | 174.032 | 26.880    | 18.603     | 7.180  | 141.932     | 69.820    | 82.310          | 29.445          | 79.623              |
| 1009 | 174.429 | 27.252    | 18.522     | 4.167  | 148.478     | 69.887    | 79.930          | 30.556          | 81.334              |
| 1409 | 175.228 | 28.012    | 18.355     | 4.900  | 161.213     | 70.021    | 73.374          | 30.069          | 82.128              |
| 1404 | 176.295 | 29.051    | 18.125     | 5.118  | 162.367     | 70.198    | 74.158          | 30.312          | 84.253              |
| 809  | 177.029 | 29.782    | 17.961     | 3.811  | 162.720     | 70.318    | 74.323          | 30.097          | 85.466              |
| 1221 | 177.420 | 30.177    | 17.872     | 6.968  | 146.364     | 70.382    | 86.720          | 31.201          | 87.382              |
| 702  | 177.902 | 30.670    | 17.760     | 3.799  | 145.938     | 70.461    | 84.967          | 29.552          | 86.790              |
| 1010 | 178.557 | 31.349    | 17.603     | 4.090  | 151.355     | 70.567    | 82.156          | 29.861          | 88.641              |
| 1200 | 180.613 | 33.553    | 17.078     | 5.694  | 148.814     | 70.895    | 88.923          | 30.420          | 95.067              |
| 1217 | 181.034 | 34.018    | 16.963     | 6.825  | 149.125     | 70.961    | 89.202          | 30.254          | 96.349              |
| 703  | 181.645 | 34.702    | 16.790     | 3.688  | 150.564     | 71.057    | 89.496          | 30.451          | 98.844              |
| 1011 | 182.572 | 35.759    | 16.516     | 3.940  | 156.745     | 71.201    | 86.983          | 31.025          | 103.442             |
| 1222 | 184.222 | 37.703    | 15.976     | 6.616  | 154.219     | 71.454    | 94.445          | 31.451          | 113.330             |
| 704  | 185.271 | 38.982    | 15.588     | 3.549  | 156.464     | 71.613    | 95.503          | 31.421          | 121.769             |
| 1201 | 186.127 | 40.030    | 15.236     | 5.329  | 158.456     | 71.742    | 98.948          | 32.509          | 132.153             |
| 1012 | 187.577 | 41.915    | 14.580     | 6.026  | 151.278     | 71.957    | 80.630          | 16.306          | 141.359             |
| 1218 | 187.633 | 41.988    | 14.499     | 6.358  | 160.079     | 71.965    | 100.540         | 30.050          | 156.489             |

## 4. Results

The specific heat of the saturated liquid was measured for 66 temperatures. The lowest was 95 K (triple point, 90.68 K) and the highest 187 K (see fig. 2 and table 1). The estimated uncertainty in the measured value of  $C_\sigma$  is about 0.5 percent generally but increasing to about 5 percent within a few Kelvin of the critical point. The data of Weibe and Breevort [12] are shown for comparison as the closed circles. Their measurements agree remarkably well with the new data, considering the state of the art at that time.

Figure 3 and table 2 show  $C_V$  as a function of temperature for the various isochores. The dashed line is the locus of  $C_V$  for saturated liquid as extrapolated from the  $C_V$  measurements. The uncertainties in  $C_V$  are the same as for  $C_\sigma$ . Densities  $Q$ ,  $R$ ,  $S$ , and  $T$  have uncertainties as large as 5 percent near critical temperature, indicated as  $T_c$  on figure 3. Density  $T$  is 22 percent less than critical density.

Figure 4 shows  $C_V$  at saturation. The circles are values extrapolated from the  $C_V$  data and the triangles are computed from  $C_\sigma$  data by adding the term  $T \left( \frac{\partial P}{\partial T} \right)_v \frac{dV}{dT}$ . These derivatives, evaluated analytically from a representation of the  $PVT$  surface [2], introduce the scatter and the lowering of the values from the extrapolated values which have essentially the same accuracy as the measured  $C_V$  values.

Comparison was made with the  $C_p$  data of Jones et al. [17] on their 2000 lb/in<sup>2</sup> (136.7 bar) by interpolation of the  $C_V$  data and adding the  $PVT$  contribution. Figure 5 shows the close agreement of the two sets of data. The other curve is calculated from spectroscopic heat capacities together with the  $PVT$  term above critical temperature, ( $T_c$ ). Below the critical temperature, latent heats must also be used. The discontinuity is, of course, at  $T_c$ .



TABLE 2. Specific heat at constant volume,  $C_v$ , of methane; heat correction for calorimeter expansion  $C_1$ , heat capacity of empty calorimeter,  $C_0$ , total heat capacity of calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $DT$

| ID   | Temp<br>K | Press<br>bar | Den<br>mol/l | DT<br>K | DQ/DT<br>J/K | C <sub>0</sub><br>J/K | C <sub>1</sub><br>J/mol · K | C <sub>T</sub><br>J/mol · K |
|------|-----------|--------------|--------------|---------|--------------|-----------------------|-----------------------------|-----------------------------|
| 2209 | 200.342   | 56.917       | 7.991        | 7.542   | 94.477       | 73.734                | 0.166                       | 35.351                      |
| 2203 | 201.339   | 58.027       | 7.991        | 5.459   | 94.406       | 73.865                | .167                        | 35.004                      |
| 2210 | 207.854   | 65.217       | 7.988        | 7.559   | 94.152       | 74.691                | .170                        | 33.153                      |
| 2204 | 208.168   | 65.562       | 7.988        | 7.419   | 94.184       | 74.729                | .170                        | 33.141                      |
| 2211 | 215.402   | 73.451       | 7.984        | 7.554   | 94.227       | 75.593                | .175                        | 31.732                      |
| 2212 | 222.937   | 81.598       | 7.980        | 7.511   | 94.677       | 76.439                | .182                        | 31.046                      |
| 2205 | 222.993   | 81.658       | 7.980        | 7.361   | 94.691       | 76.445                | .182                        | 31.059                      |
| 2206 | 230.373   | 89.583       | 7.977        | 7.387   | 95.264       | 77.226                | .189                        | 30.698                      |
| 2213 | 230.453   | 89.668       | 7.977        | 7.484   | 95.130       | 77.234                | .189                        | 30.455                      |
| 2207 | 237.534   | 97.229       | 7.973        | 7.324   | 95.819       | 77.940                | .195                        | 30.419                      |
| 2214 | 238.128   | 97.862       | 7.973        | 7.382   | 95.748       | 77.998                | .196                        | 30.198                      |
| 2208 | 244.733   | 104.881      | 7.970        | 7.292   | 96.283       | 78.619                | .202                        | 30.045                      |
| 2215 | 245.476   | 105.669      | 7.969        | 7.369   | 96.374       | 78.687                | .203                        | 30.084                      |
| 2216 | 252.815   | 113.433      | 7.966        | 7.332   | 97.017       | 79.335                | .210                        | 30.067                      |
| 2218 | 266.349   | 127.671      | 7.959        | 7.246   | 97.960       | 80.436                | .222                        | 29.785                      |
|      |           |              |              |         |              |                       |                             |                             |
| 1505 | 195.780   | 53.853       | 10.176       | 6.728   | 102.498      | 73.123                | .185                        | 39.325                      |
| 1523 | 198.095   | 57.310       | 10.175       | 5.257   | 101.084      | 73.436                | .189                        | 36.999                      |
| 1521 | 198.426   | 57.804       | 10.174       | 5.284   | 101.071      | 73.480                | .189                        | 36.921                      |
| 1506 | 202.601   | 64.048       | 10.171       | 6.923   | 100.060      | 74.028                | .194                        | 34.818                      |
| 1502 | 203.142   | 64.857       | 10.171       | 6.470   | 106.980      | 74.098                | .195                        | 44.032                      |
| 1524 | 203.375   | 65.206       | 10.171       | 5.301   | 100.142      | 74.128                | .196                        | 34.793                      |
| 1522 | 203.731   | 65.739       | 10.171       | 5.320   | 99.881       | 74.173                | .197                        | 34.382                      |
| 1525 | 208.704   | 73.193       | 10.167       | 5.334   | 99.538       | 74.795                | .203                        | 33.078                      |
| 1523 | 209.057   | 73.722       | 10.167       | 5.326   | 99.856       | 74.838                | .204                        | 33.447                      |
| 1507 | 209.526   | 74.426       | 10.166       | 6.942   | 99.491       | 74.895                | .203                        | 32.879                      |
| 1503 | 209.853   | 74.915       | 10.166       | 6.955   | 99.636       | 74.935                | .204                        | 33.020                      |
| 1526 | 214.044   | 81.206       | 10.164       | 5.346   | 99.736       | 75.434                | .211                        | 32.476                      |
| 1508 | 216.467   | 84.845       | 10.161       | 6.956   | 99.479       | 75.715                | .213                        | 31.750                      |
| 1504 | 216.813   | 85.365       | 10.161       | 6.945   | 99.842       | 75.755                | .214                        | 32.185                      |
| 1509 | 223.396   | 95.256       | 10.157       | 6.923   | 99.937       | 76.489                | .223                        | 31.318                      |
| 1510 | 230.790   | 106.373      | 10.151       | 6.920   | 100.066      | 77.268                | .233                        | 30.432                      |
| 1511 | 237.756   | 116.844      | 10.147       | 6.901   | 100.143      | 77.962                | .242                        | 29.998                      |
| 1512 | 244.636   | 127.181      | 10.142       | 6.864   | 100.993      | 78.610                | .251                        | 29.857                      |
| 1513 | 251.488   | 137.466      | 10.137       | 6.819   | 101.457      | 79.221                | .261                        | 29.650                      |
| 1514 | 259.403   | 149.331      | 10.131       | 6.782   | 102.116      | 79.886                | .271                        | 29.632                      |
| 1515 | 266.154   | 159.433      | 10.126       | 6.725   | 102.604      | 80.421                | .280                        | 29.560                      |
| 1517 | 282.516   | 183.843      | 10.114       | 6.617   | 104.067      | 81.599                | .301                        | 29.922                      |
| 1518 | 289.146   | 193.696      | 10.110       | 6.625   | 104.538      | 82.032                | .310                        | 29.964                      |
| 1519 | 295.822   | 203.596      | 10.105       | 6.556   | 105.109      | 82.444                | .319                        | 30.170                      |
|      |           |              |              |         |              |                       |                             |                             |
| 219  | 195.627   | 55.318       | 11.838       | 9.621   | 105.430      | 73.102                | .204                        | 37.165                      |
| 223  | 196.581   | 57.055       | 11.839       | 7.285   | 104.709      | 73.232                | .209                        | 36.177                      |
| 224  | 203.924   | 70.601       | 11.832       | 7.393   | 103.134      | 74.198                | .226                        | 33.223                      |
| 225  | 211.370   | 84.550       | 11.826       | 7.394   | 102.930      | 75.118                | .242                        | 31.908                      |
| 205  | 215.626   | 92.584       | 11.822       | 8.023   | 102.779      | 75.618                | .250                        | 31.148                      |
| 226  | 218.787   | 98.572       | 11.819       | 7.411   | 102.950      | 75.979                | .256                        | 30.922                      |
| 206  | 223.653   | 107.819      | 11.815       | 8.022   | 103.224      | 76.517                | .265                        | 30.609                      |
| 227  | 226.191   | 112.653      | 11.813       | 7.374   | 103.274      | 76.789                | .270                        | 30.347                      |

TABLE 2. Specific heat at constant volume,  $C_v$ , of methane; heat correction for calorimeter expansion  $C_1$ , heat capacity of empty calorimeter,  $C_0$ , total heat capacity of calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $DT$ —Continued

| ID  | Temp<br>K | Press<br>bar | Den<br>mol/l | $DT$<br>K | $DQ/DT$<br>J/K | $C_0$<br>J/K | $C_1$<br>J/mol · K | $C_v$<br>J/mol · K |
|-----|-----------|--------------|--------------|-----------|----------------|--------------|--------------------|--------------------|
| 207 | 231.675   | 123.117      | 11.808       | 7.947     | 103.685        | 77.359       | 0.279              | 30.155             |
| 228 | 233.566   | 126.729      | 11.806       | 7.338     | 103.858        | 77.549       | .283               | 30.130             |
| 208 | 239.625   | 138.319      | 11.801       | 7.906     | 104.383        | 78.141       | .293               | 30.043             |
| 229 | 204.923   | 140.803      | 11.800       | 7.311     | 104.171        | 78.264       | .296               | 29.653             |
| 209 | 248.734   | 155.761      | 11.792       | 7.882     | 104.855        | 78.979       | .309               | 29.604             |
| 210 | 257.453   | 172.459      | 11.784       | 9.556     | 105.552        | 79.726       | .323               | 29.534             |
| 211 | 266.957   | 190.643      | 11.775       | 9.438     | 106.408        | 80.482       | .339               | 29.632             |
| 212 | 276.534   | 208.934      | 11.766       | 9.341     | 107.186        | 81.187       | .355               | 29.702             |
| 214 | 296.364   | 246.647      | 11.748       | 9.271     | 108.845        | 82.476       | .388               | 30.098             |
| 301 | 204.751   | 77.746       | 13.088       | 7.244     | 105.556        | 74.303       | .264               | 32.393             |
| 302 | 212.016   | 93.924       | 13.080       | 7.229     | 105.596        | 75.195       | .282               | 31.485             |
| 303 | 219.265   | 110.242      | 13.073       | 7.214     | 105.859        | 76.033       | .299               | 30.868             |
| 304 | 226.524   | 126.697      | 13.065       | 7.179     | 106.293        | 76.824       | .315               | 30.478             |
| 305 | 234.072   | 143.881      | 13.057       | 7.166     | 106.784        | 77.600       | .331               | 30.165             |
| 306 | 241.245   | 160.256      | 13.050       | 7.146     | 107.321        | 78.295       | .347               | 29.985             |
| 307 | 248.387   | 176.580      | 13.042       | 7.078     | 107.969        | 78.948       | .362               | 29.965             |
| 309 | 262.566   | 208.987      | 13.026       | 7.007     | 109.144        | 80.140       | .391               | 29.918             |
| 310 | 276.780   | 241.398      | 13.011       | 6.874     | 110.608        | 81.204       | .419               | 30.309             |
| 313 | 276.944   | 241.772      | 13.010       | 6.908     | 110.434        | 81.216       | .419               | 30.114             |
| 314 | 283.783   | 257.318      | 13.003       | 6.854     | 110.947        | 81.684       | .433               | 30.147             |
| 311 | 290.591   | 272.756      | 12.995       | 6.847     | 111.617        | 82.124       | .446               | 30.375             |
| 312 | 297.427   | 288.216      | 12.987       | 6.788     | 112.344        | 82.540       | .460               | 30.687             |
| 501 | 191.539   | 52.228       | 14.388       | 7.056     | 108.595        | 72.531       | .268               | 34.042             |
| 528 | 195.039   | 61.226       | 14.383       | 8.352     | 107.756        | 73.021       | .281               | 32.765             |
| 502 | 198.638   | 70.602       | 14.379       | 7.127     | 107.453        | 73.509       | .295               | 32.600             |
| 520 | 200.323   | 75.028       | 14.377       | 8.432     | 107.534        | 73.732       | .299               | 31.860             |
| 503 | 205.816   | 89.577       | 14.371       | 7.131     | 107.532        | 74.437       | .315               | 31.171             |
| 521 | 208.733   | 97.366       | 14.366       | 8.358     | 107.655        | 74.799       | .321               | 30.940             |
| 504 | 212.954   | 108.696      | 14.362       | 7.102     | 107.804        | 75.306       | .334               | 30.585             |
| 522 | 217.103   | 119.884      | 14.356       | 8.319     | 107.990        | 75.788       | .347               | 30.292             |
| 505 | 220.066   | 127.901      | 14.353       | 7.075     | 108.187        | 76.123       | .356               | 30.152             |
| 523 | 225.394   | 142.360      | 14.346       | 8.245     | 108.656        | 76.704       | .369               | 30.632             |
| 506 | 227.167   | 147.180      | 14.344       | 7.039     | 108.887        | 76.892       | .375               | 30.067             |
| 524 | 234.287   | 166.574      | 14.334       | 8.234     | 109.380        | 77.621       | .392               | 29.826             |
| 507 | 234.417   | 166.928      | 14.335       | 6.969     | 109.372        | 77.634       | .393               | 29.805             |
| 508 | 241.372   | 185.902      | 14.326       | 6.927     | 109.898        | 78.307       | .411               | 29.647             |
| 525 | 242.493   | 188.962      | 14.324       | 8.159     | 109.939        | 78.412       | .412               | 29.585             |
| 509 | 248.293   | 204.791      | 14.317       | 6.910     | 110.378        | 78.940       | .428               | 29.485             |
| 510 | 255.197   | 223.622      | 14.308       | 6.870     | 111.009        | 79.538       | .445               | 29.500             |
| 511 | 262.143   | 242.543      | 14.299       | 6.820     | 111.759        | 80.107       | .461               | 29.656             |
| 514 | 265.537   | 251.779      | 14.294       | 7.970     | 112.059        | 80.373       | .468               | 29.691             |
| 512 | 269.538   | 262.650      | 14.289       | 7.971     | 112.383        | 80.678       | .478               | 29.689             |
| 515 | 273.495   | 273.386      | 14.284       | 7.928     | 112.890        | 80.969       | .487               | 29.885             |
| 513 | 277.494   | 284.223      | 14.278       | 7.914     | 113.176        | 81.255       | .497               | 29.877             |
| 516 | 281.439   | 294.892      | 14.273       | 7.875     | 113.651        | 81.527       | .506               | 30.061             |
| 517 | 289.349   | 316.229      | 14.262       | 7.793     | 114.710        | 82.045       | .524               | 30.557             |



TABLE 2. Specific heat at constant volume,  $C_v$ , of methane; heat correction for calorimeter expansion  $C_1$ , heat capacity of empty calorimeter,  $C_0$ , total heat capacity of calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $DT$  — Continued

| ID   | Temp<br>K | Press<br>bar | Den<br>mol/l | DT<br>K | DQ/DT<br>J/K | C0<br>J/K | C1<br>J/mol · K | C <sub>v</sub><br>J/mol · K |
|------|-----------|--------------|--------------|---------|--------------|-----------|-----------------|-----------------------------|
| 701  | 187.947   | 51.088       | 16.104       | 7.172   | 110.110      | 72.012    | 0.350           | 32.038                      |
| 707  | 188.669   | 53.498       | 16.103       | 6.957   | 110.164      | 72.118    | .353            | 31.990                      |
| 721  | 191.577   | 63.245       | 16.098       | 6.895   | 110.072      | 72.537    | .367            | 31.543                      |
| 702  | 195.118   | 75.188       | 16.093       | 7.178   | 110.019      | 73.032    | .378            | 31.066                      |
| 708  | 195.637   | 76.943       | 16.092       | 6.947   | 110.062      | 73.103    | .380            | 31.040                      |
| 720  | 199.140   | 88.833       | 16.087       | 6.859   | 110.111      | 73.576    | .390            | 30.670                      |
| 703  | 202.277   | 99.525       | 16.082       | 7.135   | 110.530      | 73.987    | .397            | 30.670                      |
| 709  | 202.632   | 100.738      | 16.082       | 6.943   | 110.308      | 74.032    | .399            | 30.441                      |
| 704  | 209.408   | 123.943      | 16.071       | 7.112   | 110.909      | 74.881    | .426            | 30.204                      |
| 710  | 209.569   | 124.495      | 16.071       | 6.933   | 110.994      | 74.901    | .427            | 30.258                      |
| 711  | 216.494   | 148.306      | 16.060       | 6.873   | 111.429      | 75.718    | .450            | 29.911                      |
| 705  | 216.509   | 148.360      | 16.060       | 7.078   | 111.388      | 75.720    | .450            | 29.875                      |
| 712  | 223.352   | 171.937      | 16.049       | 6.816   | 112.095      | 76.484    | .472            | 29.805                      |
| 706  | 223.990   | 173.825      | 16.048       | 7.007   | 112.128      | 76.544    | .473            | 29.780                      |
| 713  | 230.437   | 196.359      | 16.038       | 6.824   | 112.675      | 77.232    | .494            | 29.639                      |
| 714  | 237.251   | 219.833      | 16.027       | 6.791   | 113.485      | 77.913    | .515            | 29.729                      |
| 715  | 244.048   | 243.213      | 16.016       | 6.758   | 113.994      | 78.556    | .536            | 29.594                      |
| 716  | 250.777   | 266.302      | 16.005       | 6.660   | 114.660      | 79.159    | .557            | 29.627                      |
| 717  | 257.424   | 289.044      | 15.994       | 6.627   | 115.322      | 79.724    | .577            | 29.689                      |
| 718  | 264.035   | 311.587      | 15.983       | 6.571   | 116.177      | 80.256    | .597            | 29.944                      |
| 719  | 270.623   | 333.970      | 15.972       | 6.544   | 116.590      | 80.759    | .616            | 29.849                      |
| 1601 | 185.501   | 42.477       | 16.038       | 2.172   | 110.226      | 71.648    | .337            | 32.608                      |
| 1602 | 187.587   | 49.323       | 16.035       | 2.006   | 110.069      | 71.959    | .348            | 32.198                      |
| 1603 | 189.591   | 55.934       | 16.032       | 2.009   | 109.944      | 72.252    | .358            | 31.832                      |
| 1604 | 191.595   | 62.582       | 16.029       | 2.004   | 110.119      | 72.539    | .361            | 31.732                      |
| 1618 | 192.871   | 66.824       | 16.024       | 6.135   | 109.928      | 72.719    | .367            | 31.410                      |
| 1605 | 193.605   | 69.272       | 16.026       | 2.010   | 109.753      | 72.822    | .377            | 31.163                      |
| 1606 | 195.615   | 75.989       | 16.023       | 2.012   | 109.895      | 73.100    | .383            | 31.041                      |
| 1607 | 197.622   | 82.719       | 16.020       | 2.003   | 110.311      | 73.373    | .389            | 31.157                      |
| 1608 | 199.628   | 89.464       | 16.017       | 2.005   | 110.203      | 73.640    | .396            | 30.831                      |
| 1619 | 200.031   | 90.821       | 16.011       | 8.252   | 110.152      | 73.693    | .391            | 30.746                      |
| 1620 | 209.230   | 121.946      | 15.996       | 10.164  | 110.765      | 74.859    | .419            | 30.246                      |
| 1609 | 217.884   | 151.399      | 15.986       | 6.097   | 111.290      | 75.877    | .452            | 29.793                      |
| 1611 | 223.224   | 169.616      | 15.977       | 6.069   | 111.946      | 76.470    | .469            | 29.830                      |
| 1610 | 223.903   | 171.930      | 15.976       | 6.052   | 112.026      | 76.544    | .471            | 29.834                      |
| 1622 | 229.421   | 190.764      | 15.964       | 10.032  | 112.633      | 77.128    | .484            | 29.812                      |
| 1612 | 229.453   | 190.871      | 15.967       | 6.063   | 112.588      | 77.131    | .488            | 29.795                      |
| 1623 | 239.424   | 224.878      | 15.948       | 9.937   | 113.475      | 78.122    | .515            | 29.681                      |
| 1613 | 241.503   | 231.959      | 15.948       | 5.956   | 113.763      | 78.319    | .525            | 29.718                      |
| 1614 | 247.521   | 252.433      | 15.939       | 5.898   | 114.293      | 78.871    | .544            | 29.715                      |
| 1615 | 253.443   | 272.535      | 15.929       | 5.912   | 114.868      | 79.389    | .562            | 29.712                      |
| 1616 | 259.333   | 292.473      | 15.919       | 5.842   | 115.529      | 79.880    | .579            | 29.869                      |
| 1617 | 265.198   | 312.270      | 15.910       | 5.849   | 116.001      | 80.347    | .597            | 29.856                      |

TABLE 2. Specific heat at constant volume,  $C_v$ , of methane; heat correction for calorimeter expansion Cl, heat capacity of empty calorimeter,  $C_0$ , total heat capacity of calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $DT$ —Continued

| ID   | Temp<br>K | Press<br>bar | Den<br>mol/l | $DT$<br>K | $DQ/DT$<br>J/K | $C_0$<br>J/K | Cl<br>J/mol · K | $C_r$<br>J/mol · K |
|------|-----------|--------------|--------------|-----------|----------------|--------------|-----------------|--------------------|
| 1309 | 184.764   | 45.449       | 16.723       | 5.354     | 110.741        | 71.537       | 0.381           | 31.721             |
| 1301 | 187.826   | 56.698       | 16.717       | 6.932     | 110.769        | 71.994       | .394            | 31.357             |
| 1310 | 190.103   | 65.099       | 16.714       | 5.347     | 110.862        | 72.326       | .406            | 31.150             |
| 1302 | 194.733   | 82.255       | 16.706       | 6.892     | 110.968        | 72.979       | .423            | 30.685             |
| 1311 | 195.445   | 84.904       | 16.706       | 5.344     | 111.063        | 73.077       | .427            | 30.679             |
| 1303 | 201.094   | 105.956      | 16.696       | 5.855     | 111.252        | 73.833       | .446            | 30.196             |
| 1323 | 202.937   | 112.841      | 16.693       | 6.031     | 111.551        | 74.072       | .453            | 30.239             |
| 1312 | 206.062   | 124.532      | 16.688       | 5.287     | 111.919        | 74.468       | .465            | 30.204             |
| 1304 | 206.122   | 124.756      | 16.689       | 4.249     | 111.707        | 74.475       | .466            | 30.023             |
| 1324 | 208.680   | 134.336      | 16.683       | 5.477     | 112.228        | 74.792       | .473            | 30.184             |
| 1305 | 210.401   | 140.788      | 16.681       | 4.330     | 112.079        | 75.001       | .481            | 29.882             |
| 1313 | 211.348   | 144.339      | 16.679       | 5.286     | 112.322        | 75.115       | .483            | 29.987             |
| 1325 | 214.143   | 154.818      | 16.674       | 5.464     | 112.494        | 75.446       | .492            | 29.847             |
| 1306 | 215.024   | 158.123      | 16.673       | 4.934     | 112.592        | 75.549       | .496            | 29.840             |
| 1314 | 216.658   | 164.252      | 16.670       | 5.219     | 112.889        | 75.737       | .501            | 29.924             |
| 1326 | 219.582   | 175.218      | 16.665       | 5.433     | 112.992        | 76.069       | .511            | 29.727             |
| 1327 | 225.003   | 195.545      | 16.655       | 5.423     | 113.635        | 76.662       | .530            | 29.749             |
| 1317 | 232.337   | 223.009      | 16.643       | 5.178     | 114.228        | 77.426       | .555            | 29.585             |
| 1318 | 237.657   | 242.891      | 16.633       | 5.448     | 114.856        | 77.952       | .572            | 29.651             |
| 1319 | 243.097   | 263.174      | 16.624       | 5.401     | 115.579        | 78.468       | .590            | 29.802             |
| 1320 | 248.519   | 283.339      | 16.614       | 5.387     | 115.951        | 78.960       | .608            | 29.686             |
| 1321 | 253.921   | 303.370      | 16.604       | 5.359     | 116.619        | 79.430       | .626            | 29.831             |
| 1322 | 259.304   | 323.264      | 16.595       | 5.339     | 117.189        | 79.878       | .644            | 29.913             |
| 411  | 187.325   | 58.469       | 17.007       | 8.019     | 111.229        | 71.920       | .416            | 31.221             |
| 401  | 193.924   | 83.993       | 16.997       | 6.900     | 111.328        | 72.867       | .443            | 30.513             |
| 406  | 196.587   | 94.337       | 16.992       | 7.437     | 111.563        | 73.233       | .452            | 30.399             |
| 413  | 203.953   | 123.025      | 16.973       | 7.970     | 112.216        | 74.202       | .478            | 30.119             |
| 414  | 211.983   | 154.390      | 16.964       | 7.898     | 113.134        | 75.192       | .507            | 30.033             |
| 415  | 219.901   | 185.282      | 16.950       | 7.850     | 113.769        | 76.104       | .535            | 29.782             |
| 416  | 227.768   | 215.952      | 16.936       | 7.807     | 114.550        | 76.955       | .562            | 29.698             |
| 417  | 235.598   | 246.397      | 16.922       | 7.735     | 115.435        | 77.751       | .590            | 29.743             |
| 418  | 245.293   | 283.931      | 16.904       | 7.650     | 116.261        | 78.670       | .623            | 29.635             |
| 419  | 252.926   | 313.338      | 16.890       | 7.598     | 117.007        | 79.345       | .649            | 29.667             |
| 1801 | 178.581   | 37.972       | 18.086       | 3.069     | 112.484        | 70.571       | .469            | 31.280             |
| 1802 | 181.649   | 51.836       | 18.080       | 3.085     | 112.625        | 71.057       | .495            | 30.991             |
| 1803 | 186.224   | 72.545       | 18.068       | 6.039     | 112.813        | 71.756       | .503            | 30.598             |
| 1804 | 192.299   | 100.083      | 18.056       | 6.060     | 113.438        | 72.639       | .530            | 30.377             |
| 1805 | 198.354   | 127.540      | 18.044       | 6.039     | 113.922        | 73.471       | .554            | 30.090             |
| 1806 | 204.379   | 154.828      | 18.032       | 6.010     | 114.564        | 74.256       | .578            | 29.958             |
| 1807 | 210.370   | 181.915      | 18.019       | 5.964     | 115.132        | 74.998       | .602            | 29.803             |
| 1808 | 216.641   | 210.187      | 18.006       | 5.923     | 115.821        | 75.735       | .627            | 29.741             |
| 1809 | 222.620   | 237.053      | 17.994       | 5.886     | 116.615        | 76.404       | .651            | 29.812             |
| 1810 | 228.488   | 263.318      | 17.982       | 5.854     | 117.179        | 77.031       | .674            | 29.742             |
| 1811 | 234.304   | 289.242      | 17.970       | 5.825     | 117.723        | 77.623       | .697            | 29.683             |
| 1812 | 240.990   | 318.901      | 17.955       | 5.797     | 118.614        | 78.271       | .723            | 29.841             |

TABLE 2. Specific heat at constant volume,  $C_v$ , of methane; heat correction for calorimeter expansion  $C_1$ ; heat capacity of empty calorimeter,  $C_0$ ; total heat capacity of calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $DT$  — Continued

| ID   | Temp<br>K | Press<br>bar | Dens<br>mol/l | DT<br>K | DQ/DT<br>J/K | $C_0$<br>J/K | $C_1$<br>J/mol · K | $C_v$<br>J/mol · K |
|------|-----------|--------------|---------------|---------|--------------|--------------|--------------------|--------------------|
| 1709 | 172.603   | 40.302       | 19.500        | 6.087   | 114.035      | 69.577       | 0.596              | 30.637             |
| 1710 | 178.550   | 73.409       | 19.436        | 6.101   | 114.965      | 70.566       | .608               | 30.586             |
| 1701 | 181.613   | 90.419       | 19.479        | 6.082   | 115.092      | 71.052       | .636               | 30.306             |
| 1711 | 184.637   | 107.182      | 19.472        | 6.065   | 115.515      | 71.517       | .650               | 30.262             |
| 1702 | 187.628   | 123.725      | 19.465        | 6.054   | 115.740      | 71.965       | .663               | 30.094             |
| 1712 | 190.680   | 140.564      | 19.457        | 6.039   | 116.187      | 72.408       | .676               | 30.082             |
| 1703 | 193.640   | 156.857      | 19.450        | 6.008   | 116.537      | 72.827       | .690               | 30.021             |
| 1713 | 196.693   | 173.622      | 19.443        | 5.997   | 116.917      | 73.247       | .704               | 29.980             |
| 1704 | 199.616   | 189.630      | 19.435        | 5.980   | 117.239      | 73.639       | .717               | 29.918             |
| 1714 | 202.661   | 206.260      | 19.428        | 5.946   | 117.740      | 74.036       | .731               | 29.976             |
| 1705 | 205.568   | 222.086      | 19.421        | 5.941   | 117.875      | 74.406       | .745               | 29.798             |
| 1715 | 208.615   | 238.633      | 19.413        | 5.927   | 118.353      | 74.784       | .759               | 29.854             |
| 1706 | 211.480   | 254.140      | 19.406        | 5.895   | 118.705      | 75.131       | .772               | 29.844             |
| 1716 | 214.522   | 270.555      | 19.398        | 5.886   | 118.998      | 75.490       | .787               | 29.783             |
| 1707 | 217.573   | 286.970      | 19.391        | 5.857   | 119.326      | 75.842       | .801               | 29.752             |
| 1717 | 220.387   | 302.058      | 19.384        | 5.842   | 119.782      | 76.158       | .814               | 29.837             |
| 1708 | 223.411   | 318.216      | 19.376        | 5.818   | 120.066      | 76.491       | .829               | 29.789             |
| 807  | 161.140   | 39.441       | 21.313        | 5.723   | 116.134      | 67.478       | .746               | 30.544             |
| 801  | 165.189   | 68.515       | 21.299        | 6.791   | 116.981      | 68.251       | .772               | 30.565             |
| 808  | 166.828   | 80.226       | 21.296        | 5.647   | 117.232      | 68.554       | .798               | 30.507             |
| 802  | 171.921   | 116.429      | 21.279        | 6.676   | 118.171      | 69.459       | .833               | 30.495             |
| 809  | 172.488   | 120.439      | 21.279        | 5.633   | 118.018      | 69.557       | .831               | 30.336             |
| 810  | 178.091   | 159.906      | 21.262        | 5.566   | 118.950      | 70.491       | .859               | 30.307             |
| 803  | 178.582   | 163.345      | 21.258        | 6.640   | 118.980      | 70.571       | .859               | 30.275             |
| 811  | 183.640   | 198.640      | 21.244        | 5.532   | 119.742      | 71.365       | .890               | 30.224             |
| 804  | 185.182   | 209.346      | 21.238        | 6.587   | 119.938      | 71.600       | .896               | 30.193             |
| 812  | 189.153   | 236.787      | 21.227        | 5.487   | 120.631      | 72.188       | .921               | 30.236             |
| 805  | 191.734   | 254.532      | 21.218        | 6.521   | 120.927      | 72.559       | .933               | 30.175             |
| 813  | 194.626   | 274.322      | 21.210        | 5.456   | 121.445      | 72.964       | .953               | 30.229             |
| 806  | 198.229   | 298.349      | 21.197        | 6.467   | 121.824      | 73.454       | .971               | 30.139             |
| 814  | 200.078   | 311.376      | 21.193        | 5.439   | 122.044      | 73.700       | .985               | 30.109             |
| 2109 | 153.984   | 30.846       | 22.126        | 4.385   | 117.420      | 66.016       | .818               | 31.040             |
| 2101 | 157.876   | 62.103       | 22.113        | 4.327   | 118.099      | 66.827       | .845               | 30.931             |
| 2102 | 162.200   | 96.526       | 22.098        | 4.314   | 118.875      | 67.684       | .927               | 30.800             |
| 2103 | 166.497   | 130.432      | 22.083        | 4.273   | 119.755      | 68.493       | .940               | 30.832             |
| 2104 | 170.767   | 163.847      | 22.069        | 4.251   | 120.349      | 69.259       | .951               | 30.716             |
| 2105 | 175.011   | 196.789      | 22.054        | 4.233   | 120.874      | 69.985       | .976               | 30.567             |
| 2106 | 179.314   | 229.914      | 22.040        | 4.211   | 121.698      | 70.683       | 1.003              | 30.615             |
| 2107 | 183.514   | 261.982      | 22.025        | 4.186   | 122.103      | 71.346       | 1.029              | 30.432             |
| 2108 | 187.701   | 293.689      | 22.011        | 4.164   | 122.834      | 71.976       | 1.056              | 30.468             |
| 1406 | 148.828   | 44.459       | 22.933        | 6.789   | 118.758      | 64.875       | 0.899              | 31.314             |
| 1407 | 155.536   | 104.131      | 22.907        | 6.633   | 120.057      | 66.344       | 1.015              | 31.098             |
| 1402 | 155.969   | 107.942      | 22.906        | 6.629   | 120.154      | 66.435       | 1.017              | 31.100             |
| 1401 | 156.936   | 116.449      | 22.900        | 7.882   | 120.264      | 66.635       | 1.020              | 31.042             |
| 1408 | 162.130   | 161.805      | 22.883        | 6.560   | 121.193      | 67.671       | 1.042              | 30.958             |
| 1403 | 162.555   | 165.498      | 22.881        | 6.564   | 121.222      | 67.753       | 1.043              | 30.925             |
| 1409 | 168.648   | 217.963      | 22.858        | 6.496   | 122.400      | 68.883       | 1.075              | 30.923             |
| 1404 | 169.076   | 221.618      | 22.856        | 6.499   | 122.320      | 68.960       | 1.078              | 30.826             |
| 1410 | 175.122   | 272.905      | 22.834        | 6.453   | 123.385      | 70.003       | 1.120              | 30.798             |
| 1405 | 175.530   | 276.347      | 22.832        | 6.440   | 123.626      | 70.071       | 1.123              | 30.898             |

TABLE 2. Specific heat at constant volume,  $C_v$ , of methane; heat correction for calorimeter expansion  $C_1$ ; heat capacity of empty calorimeter,  $C_0$ ; total heat capacity of calorimeter (full)  $\Delta Q/\Delta T$  or  $DQ/DT$ , with temperature, pressure, density, and temperature increment,  $DT$  - Continued

| ID   | Temp<br>K | Press<br>bar | Den<br>mol/l | DT<br>K | DQ/DT<br>J/K | C0<br>J/K | C1<br>J/mol · K | Cv<br>J/mol · K |
|------|-----------|--------------|--------------|---------|--------------|-----------|-----------------|-----------------|
| 2001 | 139.073   | 45.399       | 24.008       | 4.195   | 119.866      | 62.486    | 0.988           | 31.796          |
| 2002 | 143.270   | 88.569       | 23.990       | 4.184   | 120.961      | 63.554    | 1.146           | 31.655          |
| 2003 | 147.448   | 130.924      | 23.972       | 4.155   | 121.919      | 64.557    | 1.165           | 31.612          |
| 2004 | 151.599   | 172.491      | 23.954       | 4.133   | 122.597      | 65.498    | 1.191           | 31.437          |
| 2005 | 155.908   | 215.104      | 23.935       | 4.091   | 123.742      | 66.422    | 1.205           | 31.550          |
| 2006 | 160.011   | 255.209      | 23.917       | 4.084   | 124.120      | 67.256    | 1.236           | 31.258          |
| 2007 | 164.072   | 294.445      | 23.900       | 4.052   | 124.977      | 68.042    | 1.268           | 31.267          |
| 901  | 130.508   | 34.766       | 24.785       | 2.255   | 121.056      | 60.095    | 1.097           | 32.662          |
| 909  | 131.693   | 48.379       | 24.772       | 5.484   | 121.045      | 60.443    | 1.106           | 32.454          |
| 904  | 132.694   | 59.842       | 24.767       | 5.557   | 121.433      | 60.734    | 1.136           | 32.479          |
| 902  | 134.136   | 76.278       | 24.761       | 4.991   | 121.346      | 61.144    | 1.174           | 32.166          |
| 910  | 137.159   | 110.410      | 24.746       | 5.421   | 122.150      | 61.977    | 1.245           | 32.080          |
| 903  | 139.337   | 134.756      | 24.735       | 5.473   | 122.514      | 62.555    | 1.258           | 31.949          |
| 911  | 142.547   | 170.300      | 24.720       | 5.356   | 123.309      | 63.375    | 1.283           | 31.911          |
| 906  | 143.713   | 183.112      | 24.715       | 5.439   | 123.701      | 63.663    | 1.287           | 31.964          |
| 912  | 147.886   | 228.554      | 24.695       | 5.336   | 124.401      | 64.659    | 1.303           | 31.785          |
| 907  | 149.124   | 241.915      | 24.689       | 5.389   | 124.607      | 64.913    | 1.313           | 31.732          |
| 913  | 153.185   | 285.371      | 24.670       | 5.287   | 125.563      | 65.844    | 1.348           | 31.728          |
| 908  | 154.473   | 299.029      | 24.664       | 5.310   | 126.059      | 66.120    | 1.359           | 31.839          |
| 1201 | 121.160   | 64.484       | 25.872       | 3.070   | 122.005      | 57.118    | 1.274           | 33.145          |
| 1202 | 124.223   | 104.694      | 25.855       | 3.048   | 122.909      | 58.138    | 1.400           | 32.958          |
| 1203 | 127.262   | 144.001      | 25.838       | 3.035   | 123.532      | 59.107    | 1.420           | 32.757          |
| 1204 | 130.274   | 182.414      | 25.822       | 3.013   | 124.390      | 60.025    | 1.455           | 32.691          |
| 1101 | 110.867   | 44.963       | 26.655       | 5.194   | 121.731      | 53.349    | 1.309           | 33.910          |
| 1106 | 111.917   | 60.514       | 26.649       | 5.165   | 121.991      | 53.758    | 1.354           | 33.789          |
| 1103 | 111.855   | 59.603       | 26.649       | 5.215   | 121.835      | 53.734    | 1.351           | 33.724          |
| 1102 | 116.030   | 120.523      | 26.624       | 5.136   | 123.377      | 55.306    | 1.503           | 33.557          |
| 1107 | 117.051   | 135.181      | 26.618       | 5.109   | 123.607      | 55.677    | 1.510           | 33.478          |
| 1104 | 122.089   | 206.386      | 26.588       | 5.057   | 125.308      | 57.432    | 1.546           | 33.415          |
| 1108 | 122.094   | 206.453      | 26.588       | 5.051   | 125.107      | 57.434    | 1.546           | 33.311          |
| 1109 | 127.100   | 275.451      | 26.559       | 4.981   | 126.527      | 59.056    | 1.574           | 33.180          |
| 1105 | 127.123   | 275.769      | 26.558       | 5.028   | 126.592      | 59.064    | 1.574           | 33.210          |
| 1004 | 102.424   | 48.414       | 27.388       | 5.069   | 121.472      | 49.858    | 1.475           | 34.428          |
| 1001 | 105.029   | 90.948       | 27.371       | 5.078   | 122.552      | 50.974    | 1.619           | 34.267          |
| 1005 | 107.466   | 129.912      | 27.355       | 5.035   | 123.275      | 51.986    | 1.613           | 34.129          |
| 1002 | 110.058   | 170.735      | 27.338       | 4.981   | 124.205      | 53.030    | 1.637           | 34.049          |
| 1006 | 112.446   | 207.806      | 27.322       | 4.941   | 125.126      | 53.962    | 1.646           | 34.035          |
| 1003 | 115.142   | 249.013      | 27.305       | 4.914   | 126.082      | 54.979    | 1.652           | 33.999          |
| 1007 | 117.361   | 282.491      | 27.290       | 4.903   | 126.695      | 55.789    | 1.673           | 33.879          |
| 1912 | 92.592    | 40.274       | 28.164       | 3.061   | 120.491      | 45.311    | 1.351           | 35.326          |
| 1901 | 92.609    | 40.540       | 28.164       | 2.871   | 120.603      | 45.319    | 1.313           | 35.415          |
| 1907 | 93.793    | 62.384       | 28.155       | 2.873   | 121.008      | 45.899    | 1.458           | 35.186          |
| 1902 | 95.465    | 92.859       | 28.143       | 2.842   | 122.072      | 46.701    | 1.769           | 35.003          |
| 1913 | 95.634    | 95.885       | 28.141       | 3.022   | 122.178      | 46.780    | 1.765           | 35.020          |
| 1908 | 96.675    | 114.525      | 28.134       | 2.824   | 122.424      | 47.269    | 1.769           | 34.898          |
| 1903 | 98.301    | 143.313      | 28.122       | 2.807   | 123.144      | 48.020    | 1.740           | 34.913          |
| 1909 | 99.505    | 164.435      | 28.114       | 2.821   | 123.531      | 48.566    | 1.745           | 34.830          |
| 1904 | 101.123   | 192.506      | 28.102       | 2.793   | 124.316      | 49.288    | 1.768           | 34.839          |
| 1910 | 102.319   | 213.085      | 28.093       | 2.791   | 124.573      | 49.812    | 1.767           | 34.710          |
| 1905 | 103.902   | 240.032      | 28.082       | 2.749   | 125.401      | 50.495    | 1.755           | 34.793          |
| 1911 | 105.104   | 260.314      | 28.074       | 2.766   | 125.538      | 51.005    | 1.766           | 34.600          |
| 1906 | 106.655   | 286.252      | 28.063       | 2.751   | 126.307      | 51.653    | 1.781           | 34.644          |



Comparison of  $C_{p,m}$  methane, extrapolated to saturation, to several other liquids:  $F_2$  [8],  $O_2$  [6],  $KR$  [13],  $Ar$  [14], and  $Ne$  [15] is shown in figure 6. The density is reduced by the critical density. The spectroscopic heat capacity,  $C_p^0$ , is subtracted in each case. Molar specific heats are independent of reducing parameters [16]. All of the data except that for  $Ne$  correlate quite well. Presumably this departure of  $Ne$  is a result of its being more of a quantum fluid.  $H_2$  and  $He$  also depart markedly from this grouping as shown by Diller [16].

I would like to acknowledge the support of the American Gas Association. R. D. Goodwin's data of the PVT of methane were essential and his computer programs calculating the various functions and derivatives were of great help. I thank D. E. Diller for his numerous contributions. ~~The data shown in figure 6 are from his work.~~

## 5. References

- [1] The S. I. (international system) unit of pressure is the Pascal ( $1 \text{ Pa} \approx 1 \text{ N/m}^2$ ). The bar is  $10^5 \text{ Pa}$ , also  $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ ,  $1 \text{ lb/in}^2 = 6894.757 \text{ Pa}$ ,  $1 \text{ dyne/cm}^2 = 10^{-1} \text{ Pa}$ . Also one mole methane = 16.0430 g. based on the  $^{12}\text{C}$  scale and the natural isotopic abundance averages: see Remy, H., Chem. Berichte 101, 1 (1968).
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54A

FIGURE 1. Calorimeter and cryostat.

55A

FIGURE 2. Specific heat of the saturated liquid for methane, this work,  $\circ$ , the measurements of Wiebe and Breevort  $\oplus$  [12].

56A

FIGURE 3. Specific heat at constant volume of methane on isochores versus temperature.

Open and closed circles on alternate isochores are for clarity.

|               |              |              |
|---------------|--------------|--------------|
| A—28.0 mol/l, | B—27.4 mol/l | C—26.7 mol/l |
| D—25.8        | E—24.7       | F—24.0       |
| G—23.0        | H—22.1       | I—21.3       |
| J—19.5        | K—18.0       | L—17.0       |
| M—16.7        | N—16.0       | P—14.4       |
| Q—13.1        | R—13.1       | S—11.8       |
| T—7.9         |              |              |

57A

FIGURE 4.  $C_v$  of liquid methane evaluated at the liquid-gas boundary.

Extrapolation of  $C_p(\circ)$ , calculation from  $C_\sigma$  using PVT surface ( $\Delta$ ).

58A

FIGURE 5. Comparison of methane  $C_p$  from Jones, et al. ( $\circ$ —); to  $C_p$  calculated from  $C_v$  data, this work ( $\Delta$ ), and to  $C_p$  calculated from PVT data (—).

57A

FIGURE 6. Reduced specific heats versus reduced density for  $\text{CH}_4$  ( $\oplus$ ),  $\text{F}_2$  ( $\diamond$ ),  $\text{O}_2$  ( $\Delta$ ), Kr ( $\square$ ), Ar ( $\circ$ ), and Ne ( $\nabla$ ).



## APPENDIX H

*This survey provides a convenient summary of available data on liquid–vapour equilibria for systems of interest in cryogenics. An annotated bibliography of 392 references has been compiled, current to January 1973. These references have been scanned individually with few exceptions, and cross-indexed by system with notation of extent of data and other significant features. The systems included are those made up of the possible combinations of  $H_2(D_2, HD)$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $CO$ ,  $H_2S$ ,  $He(He^3)$ ,  $Ne$ ,  $Ar$ ,  $Kr$ ,  $Xe$ , and the saturated and unsaturated hydrocarbons through the  $C_4s$ .*

R-789

## Liquid–vapour equilibria research on systems of interest in cryogenics — A survey

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This paper is intended as a survey of the available experimental data for the equilibria between the liquid and vapour phases of fluid mixture systems of interest in cryogenics. These data are described in a number of different ways in the scientific literature, that is, dew- and bubble-points, total vapour pressures of solutions,  $K$ -values or equilibrium distribution coefficients, solubility of gases in liquids, Henry's constants, liquid–gas equilibria, liquid–vapour, etc. Such terms are simply related to the type of data and method of representation or are intended to clarify the relationship between critical temperatures of the included components. In this paper, the term 'liquid–vapour equilibria' is used collectively for all of the various descriptors.

This survey on liquid–vapour equilibria is only one part of an extensive compilation and evaluation effort on the important equilibrium and thermodynamic properties of low temperature mixtures. These include solid–liquid, solid–vapour, solid–liquid–vapour, liquid–liquid, liquid–vapour, and gas–gas phase equilibria, liquid densities, gas or vapour densities, enthalpies, and Joule–Thomson coefficients. A complete annotated bibliography of these properties will be published as a special NBS-Office of Standard Reference Data publication. However, there is an immediate interest in liquid–vapour equilibria data for a number of low temperature systems, such as those related to liquefied natural gas technology. Thus, it seems warranted to make this section available prior to publication of the complete bibliography.

In an earlier paper,<sup>1</sup> a review of research associated with low temperature solid–vapour equilibria was given with emphasis on the fundamental value of such studies. The present survey of low temperature liquid–vapour equilibria is a logical sequel, and many of the fundamental aspects presented in the earlier paper apply here as well. The same molecular species were considered in this survey of liquid–vapour equilibria data; however, the number was expanded to include isotopes of helium and hydrogen, additional hydrocarbon species, and hydrogen sulphide.

Thus, the information included here would be valuable to the low temperature physicist as well as to the cryogenic engineer, whose current interest may be in liquefied natural gas technology.

### Literature search

In the early phases of the fluid mixtures research programme in the NBS Cryogenics Division, an indexed bibliography of 681 references was prepared current to October 1959.<sup>2</sup> Included were references to experimental and theoretical work on phenomena and properties of selected pure components and mixtures containing these species. The components of primary interest were: hydrogen, helium, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, and propane. Oxygen, the remaining noble gas species, and other hydrocarbons were considered only when included in the primary systems. From experience in using this early bibliography, it was apparent that the scope was too broad and the number of primary components was too limited. The scope of the present effort was reduced to experimental properties of fluid mixtures only, but for an increased number of primary components. The components included here are:  $H_2(D_2, HD)$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $CO$ ,  $CO_2$ ,  $H_2S$ ,  $He(He-3)$ ,  $Ne$ ,  $Ar$ ,  $Kr$ ,  $Xe$ , and the saturated and unsaturated hydrocarbons through the  $C_4s$ . In addition, systems containing components other than those of primary interest (for example, the methane–benzene system) were not included. References in the 1959 bibliography which met these new criteria contributed significantly to the present effort.

A search of the NBS-Cryogenic Data Center computer listing for citations on properties of mixtures containing the subject molecular species resulted in approximately 1 400 citations. These were also screened in accordance with the criteria described above. Though the Cryogenic Data Center personnel expend considerable effort to attain comprehensive coverage of the literature,<sup>3</sup> all of the fluid species of interest here were not consistently subjects in their search of the literature. Specifically, the hydrocarbon species other than methane were not adequately covered. On the other hand, since the Cryogenic Data Center operation was begun just before Tech Note 56<sup>2</sup> was completed, the two sources provide comprehensive coverage for some

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## Discussion

It is important to emphasize that this survey is intended to include all references containing experimental data without judgement as to the reliability of the results given. Selection of best values for a given system is a complicated process at best, but must begin with a common method of data reduction which is most sensitive to discrepancies in the available data sets. A cursory discussion of the fundamental relationships is given here only to indicate the basis of data reduction or presentation methods. Examples of two such methods of liquid phase data reduction are given which serve to indicate the potential ease or difficulty in best value selection.

The equilibria represented here fall into two distinct categories: (1) equilibria of close-boiling systems in which the included components would be subcritical at the temperature of solution, and (2) equilibria of systems in which both subcritical and supercritical components are included. In either case, the equation of equilibrium is

$$\bar{f}_i(\text{vapour}) = \bar{f}_i(\text{liquid}) \quad (1)$$

where  $\bar{f}_i$  is the fugacity of component  $i$  in the mixture. The fugacity of  $i$  in the vapour is related to its mole fraction  $y_i$  and the pressure of solution  $\pi$  by

$$\bar{f}_i(\text{vapour}) = \bar{\varphi}_i y_i \pi \quad (2)$$

where  $\bar{\varphi}_i$  is the fugacity coefficient of  $i$  in the vapour mixture. The fugacity of  $i$  in the liquid is related to its mole fraction  $x_i$  and a standard state fugacity term  $S_i^\circ$  by

$$\bar{f}_i(\text{liquid}) = \gamma_i x_i S_i^\circ \quad (3)$$

where  $\gamma_i$  is the activity coefficient of  $i$  in the liquid mixture. The differences in the two categories of liquid-vapour equilibria are manifested in (3) in the method of normalization of  $\gamma$  and in the choice of the standard state term.

For close-boiling systems,  $\gamma$  for each component is conventionally normalized in the sense of Raoult's law (symmetric convention) such that

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \quad (4)$$

The standard state term is taken as the fugacity for the pure fluid at the temperature and pressure of solution. Thus (3) becomes

$$\bar{f}_i(\text{liquid}) = \gamma_i x_i f_i^\circ \quad (5)$$

where

$$f_i^\circ = p_i \varphi_i \exp \int_{p_i}^{\pi} \frac{v_i d\pi}{RT} \quad (6)$$

The terms  $p_i$  and  $\varphi_i$  are the pure component vapour pressure and fugacity coefficient, respectively.

It is also common practice to correct activity coefficients at the conditions of the solution to a reference state pressure  $\pi^{(R)}$  by the following relationship

$$\gamma_i = \gamma_i^{(R)} \exp \int_{\pi^{(R)}}^{\pi} \frac{\bar{v}_i d\pi}{RT} \quad (7)$$

The excess Gibbs energy, directly related to the activity coefficients by

$$g^E = \sum x_i RT \ln \gamma_i^{(R)} \quad (8)$$

is often reported in experimental papers, and in a number of cases appears to have been the primary purpose of the investigation.

For systems containing both subcritical and supercritical components, the activity coefficient of the subcritical component is still normalized in the sense of Raoult's law, but it is more convenient to normalize the activity coefficient of the supercritical component in the sense of Henry's law (unsymmetric convention) such that

$$\gamma_j^* \rightarrow 1 \text{ as } x_j \rightarrow 0 \quad (9)$$

The standard state term is taken as the infinite dilution Henry's law coefficient. Equation 3 then becomes

$$f_j(\text{liquid}) = \gamma_j^* x_j H_{j,i} \quad (10)$$

where

$$H_{j,i} = \lim_{x_j \rightarrow 0} \frac{\bar{f}_j}{x_j} \quad (11)$$

Full details of these relations and their uses are given by Prausnitz.<sup>9</sup> The brief discussion given here, however, is adequate for an understanding of the data reduction that is encountered in the literature on liquid-vapour equilibria of mixtures, and to some extent the significance of the general relationships which apply. Typical examples of reduced liquid phase data for the two categories of equilibria, taken from the bibliography of references are given in Figs 3 and 4.

Fig.3 is an example of the excess Gibbs energy for a close-boiling system,  $nH_2$ -Ne, derived from the data of two different investigations. Since this system also exhibits liquid phase separation, the data were taken from the region of complete liquid phase miscibility. This is also an example of excellent agreement between two different sets of data, which unfortunately is not the general case. Fig.4 is an example of a Henry's law reduction of data from two different investigations for a system,  $nH_2$ -Ar, containing a supercritical component. This is also an example of discordant results for which critical selection becomes extremely difficult without additional information on this particular mixture. In this case pressure has been used rather than fugacity, which is quite common. Though the data have not been reduced in the true sense of Henry's law, the infinite dilution intercepts are for practical purposes the same as the Henry's constant.

Critical evaluation of the data for a given system also will require knowledge of the best available pure fluid properties which are an inherent part of the fundamental relations discussed above. The importance of thermodynamically consistent vapour pressure data was specifically emphasized



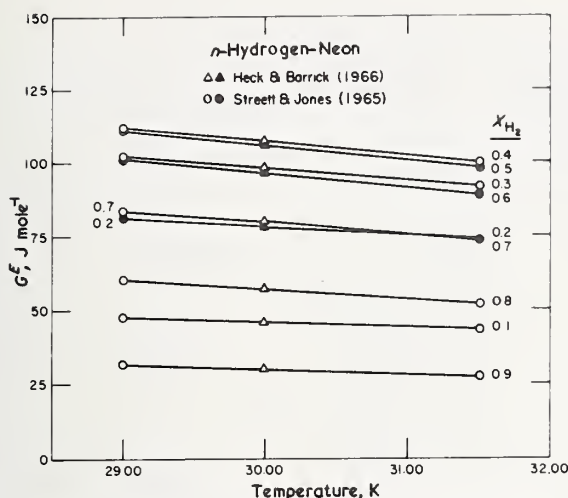


Fig.3 Excess Gibbs energy for the  $n\text{H}_2\text{--Ne}$  system as determined by Duncan and Hiza (1972) from the data of the two investigations indicated

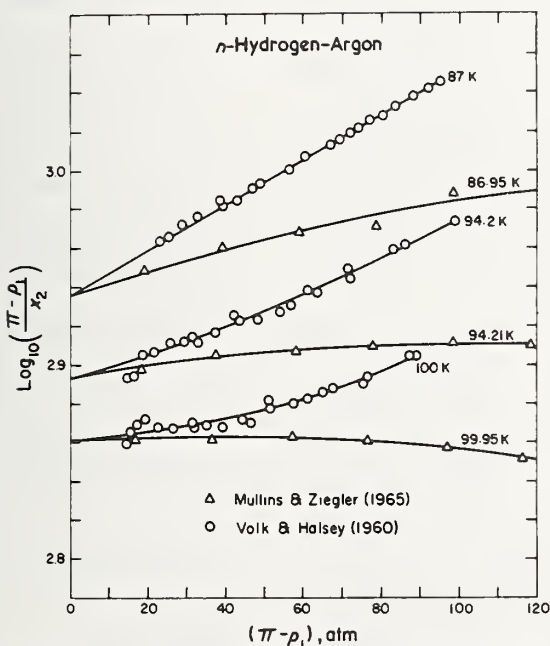


Fig.4 Gas solubility data from two investigations for the  $n\text{H}_2\text{--Ar}$  system as reduced in the sense of Henry's law by Mullins and Ziegler (1965)

in the review of solid–vapour equilibria research,<sup>1</sup> and selected references were included.

A similar list of vapour pressure references for the entire liquid region of each fluid has not been included as part of this liquid–vapour equilibria survey. However, it is worth noting several non-periodical sources of vapour pressure values and citations which are quite useful. The references to the work of W. T. Ziegler et al given in reference 1 include calculated values of vapour pressure up to the normal boiling point for most of the fluids of interest here, as well as providing a review of the available properties of the substance considered. A brief survey of vapour pressure data for the hydrocarbons not included

in those references are given in an earlier NBS Technical Note of Ziegler.<sup>10</sup> Also, the bibliography of Olien and Hall<sup>11</sup> is a valuable source of vapour pressure references for methane and the non-hydrocarbon fluids. These may still be the best available sources of vapour pressure values and citations for most of the fluids in the regions covered, but some have been definitely out-dated in part by new precise experimental measurements. Notably, the new vapour pressure measurements of Prydz and Goodwin<sup>12</sup> on methane cover the entire liquid range, and are considered by the present authors to be the best values currently available for this fluid. Nevertheless, in addition to the above sources, an examination of the literature from 1964 to the present would provide a fairly complete list of vapour pressure data references.

It is hoped that this survey of experimental liquid–vapour equilibria data for fluid mixtures of cryogenic interest includes all of the significant experimental research done prior to January 1972 and most of that done between January 1972 and January 1973. Literature searches, however, seem to approach the intended objective asymptotically. Therefore, we would welcome correspondence from those who are aware of appropriate research papers which do not appear in this survey.

The authors wish to express thanks to H. J. White Jr for his useful suggestions and discussions and to the Office of Standard Reference Data of the National Bureau of Standards for financial support. The contribution of both past and present staff members of the Cryogenic Data Center, and especially that of N. A. Olien, is gratefully acknowledged. A special acknowledgement is due to Mrs M. F. Birchfield for her painstaking typing and assistance in editing of the bibliography and tables, without which this survey would not have been possible.

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# Liquid–vapour equilibria for binary systems

| System                      | Temperature range, K | Pressure range, atm | Reference                                          | Remarks                                                      |
|-----------------------------|----------------------|---------------------|----------------------------------------------------|--------------------------------------------------------------|
| Hydrogen–helium 3           | 22–28                | 1–16                | Hiza (1972)                                        |                                                              |
| Hydrogen–helium 3           | 17–24                | 0–9                 | Matyash, Mank, Starkov (1966)                      | Pressures given as He <sup>3</sup> pressure                  |
| Hydrogen–hydrogen deuteride | 17–18                | <1                  | Hoge, Arnold (1951)                                |                                                              |
| Hydrogen–hydrogen deuteride | 20                   | 1                   | Karwat (1960)                                      |                                                              |
| Hydrogen–hydrogen deuteride | 19–27                | 0–4                 | Newman (1954)                                      | Graphs only                                                  |
| Hydrogen–hydrogen deuteride | 18–28                | 1–4                 | Newman, Jackson (1958)                             |                                                              |
| Hydrogen–hydrogen deuteride | 18–32                | 0.1–11              | Trevino (1956)                                     | Graphs only                                                  |
| Hydrogen–helium 4           | 14–16                | 1–16                | Greene (1966)                                      | Normal and para hydrogen, bubble-point                       |
| Hydrogen–helium 4           | 14–16                | 1–16                | Greene, Sonntag (1968)                             | Normal and para hydrogen, bubble-point, graphs only          |
| Hydrogen–helium 4           | 20–28                | 1–20                | Hiza (1972)                                        |                                                              |
| Hydrogen–helium 4           | 16–29                | 2–8                 | Roellig, Giese (1962)                              | Pressures given are partial                                  |
| Hydrogen–helium 4           | 17, 20, 22           | 2–58                | Smith (1952)                                       |                                                              |
| Hydrogen–helium 4           | 15–30                | 26–102              | Sneed (1966), Sneed, Sonntag, Van Wylen (1968)     | Both normal and para hydrogen, barotropic and critical locus |
| Hydrogen–helium 4           | 15–33                | 2–34                | Sonntag, Crain, Streett (1964)                     | Both normal and para hydrogen, barotropic and critical locus |
| Hydrogen–helium 4           | 20–32                | 2–34                | Sonntag, Van Wylen, Crain (1964)                   | Equilibrium hydrogen                                         |
| Hydrogen–helium 4           | 16–33                | 2–34                | Streett (1963), Streett, Sonntag, Van Wylen (1964) | Normal hydrogen                                              |
| Hydrogen–deuterium          | 4                    | —                   | Bulatova, Kogan, Lazarev (1960)                    | Qualitative data from x-ray measurements                     |
| Hydrogen–deuterium          | 19–20                | <1                  | Hoge, Arnold (1951)                                |                                                              |
| Hydrogen–deuterium          | 19                   | <1                  | Lewis, Hanson (1934)                               | Limited qualitative data graphs only                         |
| Hydrogen–deuterium          | 20–28                | 0–5                 | Newman (1954)                                      | Graphs only                                                  |
| Hydrogen–deuterium          | 18–28                | 1–4                 | Newman, Jackson (1958)                             |                                                              |
| Hydrogen–deuterium          | 18–30                | 0.1–8               | Trevino (1956)                                     | Graphs only                                                  |
| Hydrogen–neon               | 26–43                | 0–26                | Heck, Barrick (1966)                               | Normal hydrogen                                              |
| Hydrogen–neon               | 25                   | <1                  | Simon (1963b)                                      | Para hydrogen, graphs only                                   |
| Hydrogen–neon               | 25–34                | 0–14                | Streett, Jones (1965)                              | Normal hydrogen                                              |
| Hydrogen–carbon monoxide    | 83, 100, 122         | 21–238              | Akers, Eubanks (1960)                              | Graphs only                                                  |
| Hydrogen–carbon monoxide    | 32–70                | 1–50                | Dokoupil, Van Soest, Swenker (1955)                | Isobaric data, gas phase only                                |
| Hydrogen–carbon monoxide    | 83, 100, 122         | 21–238              | Eubanks (1956)                                     | Graphs only                                                  |
| Hydrogen–carbon monoxide    | 78, 83, 90           | 7–50                | Ruhemann, Tsin (1937)                              | Graphs only                                                  |
| Hydrogen–carbon monoxide    | 68–88                | 17–225              | Verschoye (1931)                                   |                                                              |



| System                   | Temperature range, K | Pressure range, atm | Reference                                   | Remarks                       |
|--------------------------|----------------------|---------------------|---------------------------------------------|-------------------------------|
| Hydrogen—carbon monoxide | 77–123               | 10–150              | Yorizane, Yoshimura, Masuoka, Toyama (1968) |                               |
| Hydrogen—nitrogen        | 83–122               | 0–170               | Akers, Eubanks (1960)                       | Graphs only                   |
| Hydrogen—nitrogen        | 63–113               | 0–200               | Charlseworth, Ruhemann (1965)               | Graphs only                   |
| Hydrogen—nitrogen        | 25–70                | 1–50                | Dokoupil, Van Soest, Swenker (1955)         | Isobaric data, gas phase only |
| Hydrogen—nitrogen        | 83, 100, 122         | 21–157              | Eubanks (1956)                              |                               |
| Hydrogen—nitrogen        | 79–109               | 13–175              | Gonikberg, Fastovskii, Gurvitsch (1939)     |                               |
| Hydrogen—nitrogen        | 90, 95               | 3–45                | Maimoni (1956) (1961)                       |                               |
| Hydrogen—nitrogen        | 77                   | 0–8                 | Matyash, Mank, Starkov (1966)               | Graphs only                   |
| Hydrogen—nitrogen        | 63–75                | 5–45                | Omar, Dokoupil (1962)                       | Isobaric data, gas phase only |
| Hydrogen—nitrogen        | 78, 83, 90           | 11–50               | Ruhemann, Tsin (1937)                       | Graphs only                   |
| Hydrogen—nitrogen        | 79–91                | <1                  | Sister, Sokolov (1940)                      |                               |
| Hydrogen—nitrogen        | 88, 90, 108, 113     | 0–110               | Stekkel, Tsin (1939a)                       | Graphs only                   |
| Hydrogen—nitrogen        | 88, 90, 108, 113     | 0–110               | Stekkel, Tsin (1939b)                       | Graphs only                   |
| Hydrogen—nitrogen        | 58–88                | 0–225               | Verschoye (1931)                            |                               |
| Hydrogen—nitrogen        | 77, 88               | <188                | Yorizane (1971)                             |                               |
| Hydrogen—nitrogen        | 77                   | 5–150               | Yorizane, Yoshimura, Masuoka, Toyama (1968) |                               |
| Hydrogen—argon           | 68–105               | 20–120              | Mullins (1965), Mullins, Ziegler (1965)     |                               |
| Hydrogen—argon           | 87–140               | 10–100              | Volk, Halsey (1960)                         |                               |
| Hydrogen—carbon dioxide  | 273–298              | —                   | Abdulayev (1939a)                           |                               |
| Hydrogen—carbon dioxide  | 298                  | 78–195              | Abdulayev (1939b)                           | Graphs only                   |
| Hydrogen—carbon dioxide  | 222, 273             | 39–242              | Greco, Casale, Negri (1954)                 |                               |
| Hydrogen—carbon dioxide  | 233–298              | 50–197              | Kaminishi, Toriumi (1966)                   |                               |
| Hydrogen—carbon dioxide  | 281, 288             | 56–106              | Mills, Miller (1945)                        |                               |
| Hydrogen—carbon dioxide  | 220–290              | 11–200              | Spano, Heck, Barrick (1968)                 |                               |
| Hydrogen—carbon dioxide  | 273                  | <370                | Yorizane (1971)                             |                               |
| Hydrogen—carbon dioxide  | 273                  | 60–370              | Yorizane, Yoshimura, Masuoka (1970)         |                               |
| Hydrogen—methane         | 117, 144, 172        | 34–272              | Benham (1956), Benham, Katz (1957)          |                               |
| Hydrogen—methane         | 90–127               | 31–227              | Fastovsky, Gonikberg (1940a, 1940b)         |                               |
| Hydrogen—methane         | 91                   | 17–205              | Freeth, Verschoye (1931)                    |                               |
| Hydrogen—methane         | 67–117               | 10–125              | Kirk (1964), Kirk, Ziegler (1965)           |                               |

| System                     | Temperature range, K | Pressure range, atm | Reference                                   | Remarks                                                            |
|----------------------------|----------------------|---------------------|---------------------------------------------|--------------------------------------------------------------------|
| Hydrogen—methane           | 158–178              | 31–78               | Levitskaya (1941)                           |                                                                    |
| Hydrogen—methane           | 158–188              | 28–83               | Likhter, Tikhovovich (1940)                 |                                                                    |
| Hydrogen—methane           | 107                  | 4–90                | Steckel, Tsing (1939a, 1939b)               | Graphs only                                                        |
| Hydrogen—methane           | 103–163              | 10–150              | Yorizane, Yoshimura, Masuoka, Toyama (1968) |                                                                    |
| Hydrogen—ethene            | 80–170               | 2–150               | Hiza, Heck, Kidnay (1968a)                  |                                                                    |
| Hydrogen—ethene            | 158–188              | 1–80                | Likhter, Tikhonovich (1939)                 |                                                                    |
| Hydrogen—ethene            | 117–255              | 17–544              | Williams, Katz (1954)                       |                                                                    |
| Hydrogen—ethane            | 144–200              | 7–136               | Cohen, Hipkin, Koppany (1967)               |                                                                    |
| Hydrogen—ethane            | 80–190               | 3–154               | Hiza, Heck, Kidnay (1968b)                  |                                                                    |
| Hydrogen—ethane            | 158–188              | 31–78               | Levitskaya (1941)                           |                                                                    |
| Hydrogen—ethane            | 139–149              | 1                   | Uehara (1932)                               |                                                                    |
| Hydrogen—ethane            | 103–283              | 17–544              | Williams, Katz (1954)                       |                                                                    |
| Hydrogen—propene           | 117–297              | 17–544              | Williams, Katz (1954)                       |                                                                    |
| Hydrogen—propane           | 278–361              | 27–497              | Burriss, Hsu, Reamer, Sage (1953)           |                                                                    |
| Hydrogen—propane           | 88–348               | 10–204              | Trust (1968), Trust, Kurata (1971)          |                                                                    |
| Hydrogen—propane           | 89–297               | 17–544              | Williams, Katz (1954)                       |                                                                    |
| Hydrogen— <i>n</i> -butane | 144–297              | 20–544              | Aroyan, Katz (1951)                         |                                                                    |
| Hydrogen— <i>n</i> -butane | 297–389              | 22–106              | Nelson, Bonnell (1943)                      |                                                                    |
| Hydrogen—isobutane         | 311–394              | 34–204              | Dean, Tooke (1946)                          |                                                                    |
| Helium 3—helium 4          | 1–2                  | —                   | Abraham, Weinstock, Osbourne (1949)         | He <sup>3</sup> —He <sup>4</sup> liquid $\lambda$ temperature only |
| Helium 3—helium 4          | 1–3                  | —                   | Daunt, Heer (1952)                          |                                                                    |
| Helium 3—helium 4          | 1.5–2.5              | <1                  | Daunt, Tseng (1955)                         | Graphs only                                                        |
| Helium 3—helium 4          | 1–3                  | —                   | Eselson (1954)                              | Graphs only                                                        |
| Helium 3—helium 4          | 1–3                  | <1                  | Eselson, Bereznyak (1954)                   | Dew-point measurement                                              |
| Helium 3—helium 4          | 1–3                  | <1                  | Eselson, Bereznyak (1956)                   | Extensive tabular data                                             |
| Helium 3—helium 4          | 1–3                  | <1                  | Eselson, Bereznyak (1955)                   | Graphs only                                                        |
| Helium 3—helium 4          | 1–2                  | —                   | Eselson, Kaganov, Lifshits (1957)           | 2nd order phase transition in He I—He II                           |
| Helium 3—helium 4          | 1                    | —                   | Eselson, Lazarev, Alekseevskii (1950)       |                                                                    |
| Helium 3—helium 4          | 2–5                  | —                   | Fairbank, Lane, Aldrich, Nier (1947)        |                                                                    |
| Helium 3—helium 4          | 2–5                  | —                   | Fairbank, Lane, Aldrich, Nier (1948)        |                                                                    |
| Helium 3—helium 4          | 1–4                  | —                   | Fairbank et al (1948)                       | Graphs only                                                        |

| System                 | Temperature range, K | Pressure range, atm | Reference                                       | Remarks               |
|------------------------|----------------------|---------------------|-------------------------------------------------|-----------------------|
| Helium 3—helium 4      | 1–2                  | <1                  | Grigorev, Eselson, Masimov et al (1968)         | Data obtained by NMR  |
| Helium 3—helium 4      | 1–2                  | <1                  | Nelson, Band (1952)                             | Graphs only           |
| Helium 3—helium 4      | 1–2                  | <1                  | Peshkov, Kachinskii (1957)                      | Dew-point measurement |
| Helium 3—helium 4      | 1–3                  | <1                  | Sreedhar, Daunt (1960)                          |                       |
| Helium 3—helium 4      | 0–2                  | <1                  | Sydoriak, Roberts (1960)                        |                       |
| Helium 3—helium 4      | 1–2                  | <1                  | Taconis, Bennakker, Nier, Aldrich (1949)        |                       |
| Helium 3—helium 4      | 1–2                  | <1                  | Wansink, Taconis, Staas (1956)                  |                       |
| Helium 3—helium 4      | 1–3                  | <1                  | Weinstock, Osborne, Abraham (1950)              | Graphs only           |
| Helium 3—deuterium     | 20–30                | 1–16                | Hiza (1972)                                     |                       |
| Helium 4—deuterium     | 20–30                | 1–20                | Hiza (1972)                                     |                       |
| Helium—neon            | 27–42                | 3–200               | Heck (1968), Heck, Barrick (1967)               |                       |
| Helium—neon            | 25–27                | 6–51                | Knorn (1967)                                    |                       |
| Helium—carbon monoxide | 77–128               | 17–136              | Sinor, Kurata (1966)                            |                       |
| Helium—nitrogen        | 83, 113              | 5–50                | Burch (1964)                                    |                       |
| Helium—nitrogen        | 78–122               | 12–68               | Buzyna, Macriss, Ellington (1963)               |                       |
| Helium—nitrogen        | 77                   | 14–68               | Davis, Rodewald, Kurata (1963)                  |                       |
| Helium—nitrogen        | 77–126               | 15–98               | Davydov, Budnevich (1971)                       |                       |
| Helium—nitrogen        | 77–120               | 14–136              | Devaney, Dalton, Meeks (1963)                   |                       |
| Helium—nitrogen        | 65–125               | 10–100              | Forg, Wirtz (1970)                              | Graphs only           |
| Helium—nitrogen        | 78, 90, 109          | 1–295               | Gonikberg, Fastovsky (1940a)                    |                       |
| Helium—nitrogen        | 68–112               | 1–215               | Kharakhorin (1940)                              |                       |
| Helium—nitrogen        | 65, 69, 77           | 14–68               | Rodewald (1963), Rodewald, Davis, Kurata (1964) |                       |
| Helium—nitrogen        | 64–108               | 5–150               | Ruhemann, Fedoritenko (1937)                    | Graphs only           |
| Helium—nitrogen        | 67–90                | 6–26                | Skripka, Dykhno (1964)                          |                       |
| Helium—nitrogen        | 78–122               | 66–816              | Streett (1967)                                  |                       |
| Helium—nitrogen        | 112–162              | 1 000–10 000        | Streett, Erickson (1972)                        |                       |
| Helium—nitrogen        | 122–126              | 34–211              | Tully, Devaney, Rhodes (1971)                   |                       |
| Helium—oxygen          | 78–122               | 20, 48              | Cannon, Robson, English (1968)                  | Liquid phase only     |
| Helium—oxygen          | 70–150               | 10–200              | Herring (1964), Herring, Barrick (1965)         |                       |

| System                | Temperature range, K | Pressure range, atm | Reference                                     | Remarks           |
|-----------------------|----------------------|---------------------|-----------------------------------------------|-------------------|
| Helium-oxygen         | 77-143               | 17-136              | Sinor, Kurata (1966)                          |                   |
| Helium-oxygen         | 67-90                | 6-26                | Skripka, Dykhno (1964)                        |                   |
| Helium-oxygen         | 65-116               | <216                | Skripka, Lobanova (1971)                      |                   |
| Helium-fluorine       | 77, 120              | 0-35                | Cannon, Crane (1968)                          |                   |
| Helium-fluorine       | 78-111               | 20, 48              | Cannon, Robson, English (1968)                | Liquid phase only |
| Helium-argon          | 84-87                | <1                  | Karasz (1958), Karasz, Halsey (1958)          | Graphs only       |
| Helium-argon          | 68-108               | 20-120              | Mullins (1965), Mullins, Ziegler (1965)       |                   |
| Helium-argon          | 93-148               | 17-136              | Sinor, Kurata (1966)                          |                   |
| Helium-argon          | 91                   | 6-26                | Skripka, Dykhno (1964)                        |                   |
| Helium-argon          | 90-115               | 196-235             | Skripka, Lobanova (1971)                      |                   |
| Helium-argon          | 91-148               | 14-680              | Streett (1969)                                |                   |
| Helium-argon          | 98-160               | 218-4 080           | Streett, Hill (1971a)                         |                   |
| Helium-carbon dioxide | 253, 273, 293        | 20-139              | Burfield, Richardson, Guereca (1970)          |                   |
| Helium-carbon dioxide | 200, 220             | 80-144              | Liu (1969)                                    | Gas phase only    |
| Helium-carbon dioxide | 220-290              | 10-200              | MacKendrick, Heck, Barrick (1968)             |                   |
| Helium-krypton        | 100-150              | 3-121               | Kidney, Miller, Hiza (1971)                   |                   |
| Helium-methane        | 124-191              | 3-68                | Devaney, Rhodes, Tully (1971)                 |                   |
| Helium-methane        | 90, 106              | 30-160              | Gonikberg, Fastovsky (1940b)                  |                   |
| Helium-methane        | 95-185               | 5-203               | Heck, Hiza (1967)                             |                   |
| Helium-methane        | 91                   | 13-102              | Hiza, Kidnay (1966)                           | Gas phase only    |
| Helium-methane        | 91-150               | 5-170               | Kharakhonin (1959a)                           |                   |
| Helium-methane        | 94-192               | 68-259              | Rhodes, Devaney, Tully (1971)                 |                   |
| Helium-methane        | 93-188               | 0-136               | Sinor (1965), Sinor, Schindler, Kurata (1966) |                   |
| Helium-methane        | 95-290               | 136-10 000          | Streett, Erickson, Hill (1972)                |                   |
| Helium-methane        | 91-124               | 0-67                | Tully, Devaney, Rhodes (1971)                 |                   |
| Helium-ethene         | 144-228              | 20-48               | Cannon, Robson, English (1968)                | Liquid phase only |
| Helium-ethene         | <260                 | <120                | Garber (1971)                                 |                   |
| Helium-ethene         | 91-150               | 4-130               | Hiza, Duncan (1969)                           | Gas phase only    |
| Helium-ethane         | 144-228              | 20-48               | Cannon, Robson, English (1968)                | Liquid phase only |
| Helium-ethane         | 170-290              | 9-200               | Heck (1968)                                   |                   |
| Helium-ethane         | 95-150               | 4-130               | Hiza, Duncan (1969)                           | Gas phase only    |

| System                   | Temperature range, K | Pressure range, atm | Reference                                           | Remarks                                  |
|--------------------------|----------------------|---------------------|-----------------------------------------------------|------------------------------------------|
| Helium—ethane            | 113–273              | 5–120               | Nikitina, Skripka, Gubkina (1970)                   |                                          |
| Helium—propene           | <260                 | <120                | Garber (1971)                                       |                                          |
| Helium—propane           | 172–255              | 20–48               | Cannon, Robson, English (1968)                      | Liquid phase only                        |
| Helium—propane           | 123–348              | 0–204               | Schindler, Swift, Kurata (1966)                     |                                          |
| Helium— <i>n</i> -butane | 330–426              | 10–71               | Jones, Kay (1967)                                   | Graphs only                              |
| Deuterium—neon           | 25                   | <1                  | Simon (1962)                                        | Graphs only                              |
| Deuterium—neon           | 25                   | <1                  | Simon (1963a)                                       |                                          |
| Deuterium—neon           | 25–40                | 1–21                | Streett (1968b)                                     |                                          |
| Deuterium—nitrogen       | 90, 95               | 8–67                | Maimoni (1961)                                      |                                          |
| Deuterium—argon          | 87–120               | 10–100              | Volk, Halsey (1960)                                 |                                          |
| Neon—nitrogen            | 83, 113              | 5–50                | Burch (1964)                                        |                                          |
| Neon—nitrogen            | 90                   | 8–30                | Skripka (1965)                                      | Liquid phase only                        |
| Neon—nitrogen            | 67–90                | 6–26                | Skripka, Dykhno (1964)                              |                                          |
| Neon—nitrogen            | 65–101               | 85–123              | Skripka, Lobanova (1971)                            |                                          |
| Neon—nitrogen            | 66–121               | 4–70                | Streett (1965)                                      |                                          |
| Neon—nitrogen            | 66–114               | 73–217              | Streett (1968a)                                     |                                          |
| Neon—oxygen              | 67–90                | 6–26                | Skripka, Dykhno (1964)                              |                                          |
| Neon—oxygen              | 64–118               | 176–206             | Skripka, Lobanova (1971)                            |                                          |
| Neon—oxygen              | 63–152               | 2–340               | Streett, Jones (1966)                               |                                          |
| Neon—argon               | 80–104               | 0–10                | Browning (1964)                                     | Phase boundary measurements, graphs only |
| Neon—argon               | 84–88                | <1                  | Karasz (1958), Karasz, Halsey (1958)                | Graphs only                              |
| Neon—argon               | 91                   | 6–26                | Skripka, Dykhno (1964)                              |                                          |
| Neon—argon               | 90–120               | 176–206             | Skripka, Lobanova (1971)                            |                                          |
| Neon—argon               | 84–130               | 4–71                | Streett (1965)                                      |                                          |
| Neon—argon               | 96–130               | 74–613              | Streett (1967)                                      |                                          |
| Neon—argon               | 87–94                | 63–1 020            | Streett, Hill (1971b)                               |                                          |
| Neon—krypton             | 100–150              | 3–106               | Miller, Kidnay, Hiza (1972)                         |                                          |
| Neon—methane             | 95–181               | 20–4 300            | Streett, Hill (1971c)                               |                                          |
| Neon—ethene              | 102, 122             | 7–45                | Hiza, Duncan (1969)                                 | Gas phase only                           |
| Neon—ethane              | 112, 130             | 15–33               | Hiza, Duncan (1969)                                 | Gas phase only                           |
| Carbon monoxide—nitrogen | 68                   | 0.1–0.3             | Duncan (1966), Duncan, Staveley (1966)              | Liquid phase only                        |
| Carbon monoxide—nitrogen | 84                   | 1–2                 | Pool, Saville, Herrington, Shields, Staveley (1962) | Liquid phase only                        |
| Carbon monoxide—nitrogen | 84                   | 1–2                 | Sprow, Prausnitz (1966a)                            |                                          |
| Carbon monoxide—nitrogen | 83–114               | 2–17                | Steckel (1935)                                      |                                          |
| Carbon monoxide—nitrogen | 70–122               | 0–28                | Torochesnikov (1937)                                |                                          |



| System                         | Temperature range, K | Pressure range, atm | Reference                                           | Remarks                                        |
|--------------------------------|----------------------|---------------------|-----------------------------------------------------|------------------------------------------------|
| Carbon monoxide—nitrogen       | 70–79                | 0–1                 | Verschoyle (1931)                                   |                                                |
| Carbon monoxide                | 70–122               | 0–28                | Yushkevich, Torocheshnikov (1936)                   |                                                |
| Carbon monoxide—argon          | 84                   | 0.7–1.3             | Duncan (1966), Duncan, Staveley (1966)              | Liquid phase only                              |
| Carbon monoxide—carbon dioxide | 273–298              | —                   | Abdulayev (1939a)                                   |                                                |
| Carbon monoxide—carbon dioxide | 273                  | 200                 | Abdulayev (1939b)                                   | Graphs only                                    |
| Carbon monoxide—carbon dioxide | 223–283              | 24–129              | Kaminishi, Arai, Saito, Maeda (1968)                |                                                |
| Carbon monoxide—carbon dioxide | 223–283              | 10–130              | Kaminishi, Toriumi (1968)                           | Graphs only                                    |
| Carbon monoxide—methane        | 91–124               | 0–5                 | Cheung, Wang (1964)                                 |                                                |
| Carbon monoxide—methane        | 91                   | 0–2                 | Mathot, Staveley, Young, Parsonage (1956)           | Liquid phase only                              |
| Carbon monoxide—methane        | 91                   | 1–2                 | Spro, Prausnitz (1966a)                             |                                                |
| Carbon monoxide—methane        | 114–186              | 7–48                | Toyama, Chappellear, Leland, Kobayashi (1962)       |                                                |
| Carbon monoxide—ethane         | 173–273              | 8–116               | Trust (1967), Trust, Kurata (1971)                  |                                                |
| Carbon monoxide—propene        | 311                  | 17–41               | Widdoes, Katz (1948)                                |                                                |
| Carbon monoxide—propane        | 86–128               | 0–6                 | Cheung, Wang (1964)                                 |                                                |
| Carbon monoxide—propane        | 148–323              | 7–136               | Trust (1967), Trust, Kurata (1971)                  |                                                |
| Carbon monoxide—propane        | 252–361              | 10–177              | Widdoes, Katz (1948)                                |                                                |
| Nitrogen—oxygen                | 65, 70, 78           | 0–1                 | Armstrong, Goldstein, Roberts (1955)                |                                                |
| Nitrogen—oxygen                | 77–91                | 1                   | Baly (1900)                                         |                                                |
| Nitrogen—oxygen                | 81–91                | 1                   | Cockett (1957)                                      |                                                |
| Nitrogen—oxygen                | 79–115               | 1–10                | Din (1960)                                          |                                                |
| Nitrogen—oxygen                | 77–125               | 0–30                | Dodge, Dunbar (1927)                                |                                                |
| Nitrogen—oxygen                | 63                   | 0.01–0.12           | Duncan (1966), Duncan, Staveley (1966)              | Liquid phase compositions only                 |
| Nitrogen—oxygen                | 75, 79               | 0–1                 | Inglis (1906)                                       |                                                |
| Nitrogen—oxygen                | 132–153              | 28–56               | Kuenen, Verschoyle, Van Urk (1923)                  | Condensation measurements on two mixtures      |
| Nitrogen—oxygen                | 84                   | 1–2                 | Pool, Saville, Herrington, Shields, Staveley (1962) | Liquid phase only                              |
| Nitrogen—oxygen                | 77–90                | 1–2                 | Sagenkahn, Fink (1944)                              |                                                |
| Nitrogen—oxygen                | 88–90                | 1                   | Thorogood, Haselden (1963)                          |                                                |
| Nitrogen—oxygen                | 78                   | —                   | Wilhelm, Schneider (1961)                           | Graph of excess Gibbs free energy, graphs only |
| Nitrogen—oxygen                | 78–134               | 1–26                | Wilson, Silverberg, Zellner (1965)                  |                                                |

| System                  | Temperature range, K | Pressure range, atm | Reference                                           | Remarks                                    |
|-------------------------|----------------------|---------------------|-----------------------------------------------------|--------------------------------------------|
| Nitrogen-argon          | 66-75                | <1                  | Browning (1964)                                     | Phase boundary determinations, graphs only |
| Nitrogen-argon          | 78-103               | 1-4                 | Fastovsky, Petrovsky (1956b)                        |                                            |
| Nitrogen-argon          | 74-95                | 0-2                 | Holst, Hamburger (1916a)                            |                                            |
| Nitrogen-argon          | 74-95                | 0-2                 | Holst, Hamburger (1916b)                            |                                            |
| Nitrogen-argon          | 112                  | 8-15                | Miller, Kidnay, Hiza (1973)                         |                                            |
| Nitrogen-argon          | 90-120               | 1-24                | Narinskii (1966)                                    |                                            |
| Nitrogen-argon          | 84                   | 1-2                 | Pool, Saville, Herrington, Shields, Staveley (1962) | Liquid phase only                          |
| Nitrogen-argon          | 84                   | 1-2                 | Sprow, Prausnitz (1966a)                            |                                            |
| Nitrogen-argon          | 80-115               | 1-11                | Thorpe (1968)                                       | Graphs only                                |
| Nitrogen-argon          | 72-134               | 1-26                | Wilson, Silverberg, Zellner (1965)                  |                                            |
| Nitrogen-carbon dioxide | 273-298              | —                   | Abdulayev (1939a)                                   |                                            |
| Nitrogen-carbon dioxide | 273                  | 0-181               | Abdulayev (1939b)                                   | Graphs only                                |
| Nitrogen-carbon dioxide | 233-298              | 50-125              | Kaminishi, Toriumi (1966)                           |                                            |
| Nitrogen-carbon dioxide | 223, 243, 273        | 7-100               | Kulikov (1969)                                      | Graphs only                                |
| Nitrogen-carbon dioxide | 273                  | 48-116              | Muirbrook (1964),<br>Muirbrook, Prausnitz (1965)    | Graphs only                                |
| Nitrogen-carbon dioxide | 222, 273             | 41-155              | Pollitzer, Strebel (1924)                           |                                            |
| Nitrogen-carbon dioxide | 140-190              | 5-200               | Smith (1963)                                        |                                            |
| Nitrogen-carbon dioxide | 273                  | 34-117              | Yorizane, Yoshimura, Masuoka (1970)                 |                                            |
| Nitrogen-carbon dioxide | 273                  | <117                | Yorizane (1971)                                     |                                            |
| Nitrogen-carbon dioxide | 218-273              | 12-137              | Zenner, Dana (1963)                                 |                                            |
| Nitrogen-methane        | 100-187              | 7-48                | Bloomer, Eakin, Ellington, Gami (1955)              | Graphs only                                |
| Nitrogen-methane        | 91-191               | 1-48                | Bloomer, Parent (1952), (1953)                      |                                            |
| Nitrogen-methane        | 129-179              | 34                  | Brandt, Stroud (1958)                               |                                            |
| Nitrogen-methane        | 122, 171             | 3-49                | Chang, Lu (1967)                                    |                                            |
| Nitrogen-methane        | 92-124               | 0-4                 | Cheung, Wang (1964)                                 |                                            |
| Nitrogen-methane        | 100-172              | 1-44                | Cines, Roach, Hogan, Roland (1953)                  |                                            |
| Nitrogen-methane        | 79-187               | 1-48                | Ellington, Eakin, Parent et al (1959)               |                                            |
| Nitrogen-methane        | 90-150               | 1-16                | Fastovsky, Petrovsky (1957)                         |                                            |
| Nitrogen-methane        | 80-180               | 1-103               | Forg, Wirtz (1970)                                  | Graphs only                                |
| Nitrogen-methane        | 84-89                | 0.9-2.4             | Fuks, Bellemans (1967)                              | Liquid phase only                          |
| Nitrogen-methane        | 77-109               | 1                   | McTaggart, Edwards (1919)                           |                                            |
| Nitrogen-methane        | 112                  | 2-13                | Miller, Kidnay, Hiza (1973)                         |                                            |

| System                      | Temperature range, K | Pressure range, atm | Reference                                           | Remarks                     |
|-----------------------------|----------------------|---------------------|-----------------------------------------------------|-----------------------------|
| Nitrogen—methane            | 113                  | —                   | Skripka et al (1970)                                |                             |
| Nitrogen—methane            | 91                   | 0–4                 | Sprow, Prausnitz (1966a)                            |                             |
| Nitrogen—methane            | 89–133               | 0–24                | Torochesnikov, Levius (1939)                        | Graphs only                 |
| Nitrogen—methane            | 90                   | 0–1                 | Vellinger, Pons (1943)                              | Graphs only                 |
| Nitrogen—ethene             | 144–228              | 20–48               | Cannon, Robson, English (1968)                      | Liquid phase only           |
| Nitrogen—ethane             | 144–228              | 20–48               | Cannon, Robson, English (1968)                      | Liquid phase only           |
| Nitrogen—ethane             | 122, 171             | 3–34                | Chang, Lu (1967)                                    |                             |
| Nitrogen—ethane             | 93                   | <1                  | Cheung, Wang (1964)                                 |                             |
| Nitrogen—ethane             | 101–302              | 7–126               | Ellington, Eaking, Parent et al (1959)              |                             |
| Nitrogen—ethane             | 114–133              | 18–40               | Yu, Elshayal, Lu (1969)                             |                             |
| Nitrogen—propene            | 78–91                | 0–3                 | Blagoi, Orobinskii (1965)                           |                             |
| Nitrogen—propane            | 172–255              | 20–48               | Cannon, Robson, English (1968)                      | Liquid phase only           |
| Nitrogen—propane            | 92–128               | 1–6                 | Cheung, Wang (1964)                                 |                             |
| Nitrogen—propane            | 312–365              | 41–149              | Roof, Baron (1967)                                  | Critical locus measurements |
| Nitrogen—propane            | 103–353              | 0–136               | Schindler, Swift, Kurata (1966)                     |                             |
| Nitrogen—propane            | 90                   | 0–1                 | Vellinger, Pons (1943)                              | Graphs only                 |
| Nitrogen— <i>n</i> —butane  | 311–422              | 35–287              | Akers, Atwell, Robinson (1954)                      |                             |
| Nitrogen— <i>n</i> —butane  | 311                  | 137–284             | Lehigh, McKetta (1966)                              |                             |
| Nitrogen— <i>n</i> —butane  | 311–411              | 16–231              | Roberts, McKetta (1961)                             |                             |
| Nitrogen— <i>n</i> —butane  | 294–394              | 17–131              | Sage, Budenholzer, Lacey (1940)                     |                             |
| Nitrogen— <i>n</i> —butane  | 153–273              | 5–200               | Skripka et al (1969)                                |                             |
| Nitrogen— <i>n</i> —butane  | 273, 283, 293        | 4, 6, 9, 11         | Steinbach, Steinbrecher (1966)                      |                             |
| Nitrogen—isobutane          | 248–323              | 0–100               | Ryabtsev, Khuchua (1970)                            |                             |
| Nitrogen— <i>i</i> sobutane | 273, 283, 293        | 4, 6, 9, 11         | Steinbach, Steinbrecher (1966)                      |                             |
| Oxygen—argon                | 87, 90, 95           | 1–2                 | Burbo, Ischkin (1936)                               |                             |
| Oxygen—argon                | 85–118               | 1–10                | Burn, Din (1962)                                    |                             |
| Oxygen—argon                | 90–110               | 1–3                 | Clark, Din, Robb (1953)                             |                             |
| Oxygen—argon                | 87–110               | 1–7                 | Din (1953)                                          |                             |
| Oxygen—argon                | 89–96                | 1–2                 | Fastovsky, Petrovsky (1955)                         |                             |
| Oxygen—argon                | 82                   | <1                  | Inglis (1906)                                       |                             |
| Oxygen—argon                | 90–120               | 1–12                | Narinskii (1957)                                    |                             |
| Oxygen—argon                | 84, 90               | 0–1                 | Pool, Saville, Herrington, Shields, Staveley (1962) | Liquid phase only           |

| System                              | Temperature range, K | Pressure range, atm | Reference                                               | Remarks           |
|-------------------------------------|----------------------|---------------------|---------------------------------------------------------|-------------------|
| Oxygen—argon                        | 87–97                | 1–2                 | Sagenkahn, Fink (1944)                                  |                   |
| Oxygen—argon                        | 91, 95               | 1–2                 | Wang (1960)                                             |                   |
| Oxygen—argon                        | 87–139               | 1–26                | Wilson, Silverberg, Zellner (1965)                      |                   |
| Oxygen—carbon dioxide               | 224                  | 7–142               | Fredenslund, Mollerup, Persson (1972)                   |                   |
| Oxygen—carbon dioxide               | 223–283              | 10–130              | Fredenslund, Sather (1970)                              |                   |
| Oxygen—carbon dioxide               | 233–298              | 50–125              | Kaminishi, Toriumi (1966)                               |                   |
| Oxygen—carbon dioxide               | 282–298              | 1–2                 | Keesom (1903)                                           |                   |
| Oxygen—carbon dioxide               | 273                  | 41–116              | Muirbrook (1964),<br>Muirbrook, Prausnitz (1965)        |                   |
| Oxygen—carbon dioxide               | 218–273              | 22–147              | Zenner, Dana (1963)                                     |                   |
| Oxygen—krypton                      | 94–107               | 1–4                 | Burch (1966)                                            |                   |
| Oxygen—krypton                      | 90–100               | 1–3                 | Fastovsky, Gurvich (1939a, b)                           |                   |
| Oxygen—krypton                      | 94–151               | 0–6                 | Fastovsky, Petrovsky (1956a)                            |                   |
| Oxygen—methane                      | 93–107               | 1–4                 | Hodges, Burch (1967)                                    |                   |
| Hydrogen sulphide—carbon dioxide    | 254–366              | 20–80               | Bierlein, Kay (1953)                                    |                   |
| Hydrogen sulphide—carbon dioxide    | 225–364              | 7–82                | Sobocinski, Kurata (1959)                               |                   |
| Hydrogen sulphide—carbon dioxide    | 221, 246, 273        | —                   | Steckel (1945)                                          |                   |
| Hydrogen sulphide—methane           | 167–344              | 0–136               | Kohn, Kurata (1958)                                     |                   |
| Hydrogen sulphide—methane           | 278–344              | 11–133              | Reamer, Sage, Lacey (1951)                              |                   |
| Hydrogen sulphide—ethane            | 267–355              | 17–82               | Kay, Brice (1953)                                       |                   |
| Hydrogen sulphide—propene           | 243, 273, 288        | —                   | Steckel (1945)                                          |                   |
| Hydrogen sulphide—propane           | 217–344              | 1–27                | Brewer, Rodewald, Kurata (1961)                         |                   |
| Hydrogen sulphide—propane           | 324–367              | 27, 34, 41          | Gilliland, Scheeline (1940)                             |                   |
| Hydrogen sulphide—propane           | 272–370              | 1–79                | Kay, Rambosek (1953)                                    |                   |
| Hydrogen sulphide—propane           | 243, 237, 288        | —                   | Steckel (1945)                                          |                   |
| Hydrogen sulphide— <i>n</i> -butane | 311–408              | 3–79                | Robinson, Hughes, Sondercock (1964)                     |                   |
| Argon—carbon dioxide                | 233–273              | 25–131              | Kaminishi, Arai, Saito, Maeda (1968)                    |                   |
| Argon—krypton                       | 104, 116             | 1–9                 | Davies, Duncan, Saville, Staveley (1967), Duncan (1966) | Liquid phase only |
| Argon—krypton                       | 88                   | 1                   | Schmidt (1960)                                          |                   |
| Argon—methane                       | 116                  | 1–9                 | Calado, Staveley (1972)                                 | Liquid phase only |
| Argon—methane                       | 92–124               | 0–4                 | Cheung, Wang (1964)                                     |                   |
| Argon—methane                       | 105–126              | 2–16                | Duncan, Hiza (1972)                                     |                   |

| System                    | Temperature range, K | Pressure range, atm  | Reference                                           | Remarks                                        |
|---------------------------|----------------------|----------------------|-----------------------------------------------------|------------------------------------------------|
| Methane- <i>n</i> -butane | 252–316              | 10–30                | Nederbragt (1938)                                   |                                                |
| Methane- <i>n</i> -butane | 311                  | 65–130               | Rigas, Mason, Thodos (1958)                         |                                                |
| Methane- <i>n</i> -butane | 211–411              | 2–119                | Roberts, Wang, Azarnoosh, McKetta (1962)            |                                                |
| Methane- <i>n</i> -butane | 294–394              | 2–131                | Sage, Hicks, Lacey (1940)                           |                                                |
| Methane- <i>n</i> -butane | 177                  | 5–31                 | Wang, McKetta (1964)                                |                                                |
| Methane-isobutane         | 198–293              | 5 to critical values | Barsuk, Skripka, Benyaminovich (1970)               |                                                |
| Methane-isobutane         | 311–378              | 5–114                | Olds, Sage, Lacey (1942)                            |                                                |
| Ethyne-propene            | 295–357              | 15–62                | McCurdy, Katz (1954)                                |                                                |
| Ethyne-propane            | 283–365              | 15–63                | McCurdy, Katz (1945)                                |                                                |
| Ethene-ethane             | 200, 233, 255        | 1–26                 | Hanson, Hogan, Ruchlen, Cines (1953)                |                                                |
| Ethene-ethane             | 169–273              | 0–40                 | Kharakhorin (1941)                                  |                                                |
| Ethene-ethane             | 169–273              | 0–41                 | Kharakhorin (1959b)                                 |                                                |
| Ethene-ethane             | 149–196              | 0–2                  | Moran (1959)                                        |                                                |
| Ethene-propene            | 303, 323             | <40                  | Rozhnov, Dorochinskaya (1969)                       |                                                |
| Ethane-propene            | 243–343              | 2–50                 | Lu, Newitt, Ruhemann (1941)                         |                                                |
| Ethane-propene            | 261–344              | 4–49                 | McKay, Reamer, Sage, Lacey (1951)                   |                                                |
| Ethane-propane            | 128–256              | 0–15                 | Djordjevich (1968), Djordjevich, Budenholzer (1970) |                                                |
| Ethane-propane            | 311–367              | 13–51                | Matschke, Thodos (1962)                             |                                                |
| Ethane-propane            | 255–283              | 7–27                 | Price (1957), Price, Kobayashi (1959)               |                                                |
| Ethane-propane            | 203–273              | —                    | Skripka et al (1970)                                |                                                |
| Ethane- <i>n</i> -butane  | 338, 367, 394        | 32–55                | Mehra, Thodos (1965)                                |                                                |
| Ethane-isobutane          | 203–273              | —                    | Skripka et al (1970)                                |                                                |
| Propene-propane           | 270, 298, 330        | 4–23                 | Hanson, Nelson, Hogan, Cines (1952)                 |                                                |
| Propene-propane           | —                    | —                    | Hirata, Hakuta, Onoda (1967)                        |                                                |
| Propene-propane           | —                    | —                    | Hirata, Hakuta (1968)                               |                                                |
| Propene-propane           | —                    | 22                   | Mann, Pardee, Smyth (1963)                          | Isobaric measurement, temperature not measured |
| Propene-propane           | 261–361              | 3–41                 | Reamer, Sage (1951)                                 |                                                |
| Propene-1-butene          | 278–411              | 1–46                 | Goff, Farrington, Sage (1950)                       |                                                |
| Propene-isobutane         | 315–397              | 13–41                | Gilliland, Scheeline (1940)                         |                                                |



| System                                  | Temperature range, K | Pressure range, atm | Reference                               | Remarks                            |
|-----------------------------------------|----------------------|---------------------|-----------------------------------------|------------------------------------|
| Propane—isobutene                       | 338–402              | 13–41               | Scheeline, Gilliland (1939)             |                                    |
| Propane— <i>n</i> –butane               | 333–419              | 15–42               | Kay (1940)                              |                                    |
| Propane— <i>n</i> –butane               | 311–411              | 5–42                | Nysewander et al (1940)                 |                                    |
| Propane— <i>n</i> –butane               | 253, 263, 273        | —                   | Skripka et al (1970)                    |                                    |
| Propane—isobutane                       | 267–394              | 1–39                | Hipkin (1966)                           |                                    |
| Propane—isobutane                       | 340                  | 10–24               | Hirata, Suda, Miyashita, Hoshino (1970) |                                    |
| Propane—isobutane                       | 253, 263, 273        | —                   | Skripka et al (1970)                    |                                    |
| <i>n</i> –Butane—isobutane              | —                    | —                   | Hirata, Suda (1968)                     |                                    |
| <i>n</i> –Butane—isobutane              | 353, 373             | 11                  | Yokoyama, Ohe (1971)                    |                                    |
| Hydrogen—hydrogen deuteride—deuterium   | 18–20                | <1                  | Arnold, Hoge (1950)                     | Measurement of dew-point pressures |
| Hydrogen—carbon monoxide—nitrogen       | 83, 100, 122         | 21–136              | Akers, Eubanks (1960)                   |                                    |
| Hydrogen—carbon monoxide—nitrogen       | 35–66                | 5–15                | Dokoupil, Van Soest, Swenker (1955)     |                                    |
| Hydrogen—carbon monoxide—nitrogen       | 83, 100, 122         | 21–136              | Eubanks (1956)                          |                                    |
| Hydrogen—carbon monoxide—nitrogen       | 68–88                | 30–150              | Fischer (1938)                          | Graphs only                        |
| Hydrogen—carbon monoxide—nitrogen       | 78, 83, 90           | 12–50               | Ruhemann, Tsin (1937)                   | Graphs only                        |
| Hydrogen—carbon monoxide—nitrogen       | 68–88                | 30–150              | Verschoyle (1931)                       | Graphs only                        |
| Hydrogen—carbon monoxide—carbon dioxide | 233–283              | 50–200              | Kaminishi, Arai, Saito, Maeda (1968)    |                                    |
| Hydrogen—carbon monoxide—carbon dioxide | 233–283              | 50–200              | Kaminishi, Toriumi (1968)               | Graphs only                        |
| Hydrogen—nitrogen—carbon dioxide        | 273–293              | 51–203              | Abdulayev (1941)                        |                                    |
| Hydrogen—carbon monoxide—propane        | 87                   | 32                  | Stein, Claitor, Geist (1962)            | Graphs only                        |
| Hydrogen—carbon monoxide—propane        | 88–348               | to 204              | Trust (1967)                            |                                    |
| Hydrogen—carbon monoxide—propane        | 88–348               | to 204              | Trust, Kurata (1971)                    |                                    |
| Hydrogen—nitrogen—methane               | 144                  | 34, 68              | Cosway (1958)                           |                                    |
| Hydrogen—nitrogen—methane               | 144, 200             | 34, 68              | Cosway, Katz (1959)                     |                                    |
| Hydrogen—nitrogen—methane               | 90, 108              | 10–100              | Steckel, Tsin (1939a)                   |                                    |
| Hydrogen—nitrogen—methane               | 90, 108              | 10–100              | Steckel, Tsin (1939b)                   |                                    |
| Hydrogen—methane—ethene                 | 158–188              | 30–80               | Likhter, Tikhonovich (1940)             | Graphs only                        |
| Hydrogen—methane—ethane                 | 115–255              | 2–136               | Cohen, Hipkin, Koppány (1967)           |                                    |

| System                                   | Temperature range, K | Pressure range, atm | Reference                                     | Remarks              |
|------------------------------------------|----------------------|---------------------|-----------------------------------------------|----------------------|
| Hydrogen—methane—ethane                  | 144, 200             | 34, 68              | Cosway (1958)                                 |                      |
| Hydrogen—methane—ethane                  | 144, 200             | 34, 68              | Cosway, Katz (1959)                           |                      |
| Hydrogen—methane—ethane                  | 158–188              | 30, 40, 80          | Levitskaya (1941)                             |                      |
| Hydrogen—methane—propene                 | 200                  | 34                  | Benham, Katz (1957)                           |                      |
| Hydrogen—methane—propane                 | 144–255              | 34, 68              | Benham, Katz (1957)                           |                      |
| Helium—neon—nitrogen                     | 83, 113              | 5–50                | Burch (1964)                                  |                      |
| Helium—neon—nitrogen                     | 68–78                | 7–48                | Tompkins, Geist (1963)                        | Graphs only          |
| Helium—nitrogen—methane                  | 76–130               | 14–136              | Boone, Devaney, Stroud (1963)                 |                      |
| Helium—nitrogen—methane                  | 77–164               | 7–82                | Rhodes, Stroud, Tully (1972)                  |                      |
| Helium—nitrogen—propane                  | 273                  | 34–204              | Schindler, Swift, Kurata (1966)               |                      |
| Nitrogen—oxygen—argon                    | 81–88                | 1                   | Fastovskii, Petrovskii (1957)                 |                      |
| Nitrogen—oxygen—argon                    | 90–120               | 1–23                | Narinskii (1969)                              |                      |
| Nitrogen—oxygen—argon                    | 81–96                | 1–2                 | Sagenkahn, Fink (1944)                        |                      |
| Nitrogen—oxygen—argon                    | —                    | —                   | Weishaupt (1948)                              | Graphs only          |
| Nitrogen—oxygen—argon                    | 78–137               | 1–26                | Wilson, Silverberg, Zellner (1965)            | Graphs only          |
| Nitrogen—oxygen—carbon dioxide           | 273                  | 51–104              | Muirbrook (1964), Muirbrook, Prausnitz (1965) |                      |
| Nitrogen—oxygen—carbon dioxide           | 218–273              | 52–129              | Zenner, Dana (1963)                           |                      |
| Nitrogen—argon—methane                   | 112                  | 3–13                | Miller, Kidnay, Hiza (1973)                   |                      |
| Nitrogen—argon—methane                   | 91                   | 1–4                 | Sprow, Prausnitz (1966b)                      |                      |
| Nitrogen—methane—ethane                  | 122, 171             | 2–28                | Chang, Lu (1967)                              |                      |
| Nitrogen—methane—ethane                  | 144, 200             | 34, 68              | Cosway (1958)                                 |                      |
| Nitrogen—methane—ethane                  | 144, 200             | 34, 68              | Cosway, Katz (1959)                           |                      |
| Nitrogen—methane—ethane                  | 112                  | 14                  | Lu, Yu, Poon (1969)                           | Liquid—liquid—vapour |
| Nitrogen—methane—ethane                  | 114–129              | 15–35               | Yu, Elshayal, Lu (1969)                       |                      |
| Nitrogen—methane— <i>n</i> -butane       | 311–411              | 34–204              | Roberts (1963)                                |                      |
| Nitrogen—methane— <i>n</i> -butane       | 311–411              | 34–204              | Roberts, McKetta (1963)                       |                      |
| Nitrogen—ethane—propane                  | 87                   | 0–1                 | Cheung, Wang (1964)                           |                      |
| Nitrogen—ethane— <i>n</i> -butane        | 311–411              | 34–272              | Lehigh (1965), Lehigh, McKetta (1966)         |                      |
| Nitrogen—propene—propane                 | 77                   | 0–1                 | Cheung, Wang (1964)                           |                      |
| Hydrogen sulphide—carbon dioxide—methane | 222, 239             | 20–48               | Hensel, Massoth (1964)                        |                      |
| Hydrogen sulphide—carbon dioxide—methane | 311                  | 41, 82, 103         | Robinson, Bailey (1957)                       |                      |
| Hydrogen sulphide—carbon dioxide—methane | 278, 344             | 27–109              | Robinson, Lorenzo, Macrygeorgos (1959)        |                      |

| System                                                    | Temperature range, K | Pressure range, atm | Reference                            | Remarks                                          |
|-----------------------------------------------------------|----------------------|---------------------|--------------------------------------|--------------------------------------------------|
| Hydrogen sulphide—methane— <i>n</i> -butane               | 244, 269, 311        | 27–82               | Robinson, Saxena (1966)              | Graphs only                                      |
| Hydrogen sulphide—methane— <i>n</i> -butane               | 244, 278, 311        | 27, 54, 82          | Saxena, Robinson (1969)              |                                                  |
| Argon—methane—ethane                                      | 116                  | 4–7                 | Elshayal, Lu (1971)                  |                                                  |
| Carbon dioxide—methane— <i>n</i> -butane                  | 244, 269, 311        | 27–82               | Robinson, Saxena (1966)              | Graphs only                                      |
| Carbon dioxide—methane— <i>n</i> -butane                  | 244, 278, 311        | 27, 54, 82          | Saxena, Robinson (1969)              |                                                  |
| Carbon dioxide—methane— <i>n</i> -butane                  | 177–311              | 27–116              | Wang, McKetta (1964)                 |                                                  |
| Carbon dioxide—ethene—propane                             | —                    | —                   | Shearn (1955)                        |                                                  |
| Carbon dioxide—propene—propane                            | 273, 293, 313        | 10–65               | Toyoshima, Yoshimura, Masuoka (1971) |                                                  |
| Methane—ethene—ethane                                     | 169–273              | 5–50                | Guter, Newitt, Ruhemann (1940)       |                                                  |
| Methane—ethene—ethane                                     | 159                  | ≤22                 | Hsi, Lu (1971)                       |                                                  |
| Methane—ethene—isobutane                                  | 311, 344             | 34, 68              | Benedict, Solomon, Ruben (1945)      |                                                  |
| Methane—ethane—propane                                    | 144–283              | 7–88                | Price (1957)                         |                                                  |
| Methane—ethane—propane                                    | 144–283              | 7–88                | Price, Kobayashi (1959)              |                                                  |
| Methane—ethane—propane                                    | 158–213              | 2–60                | Wichterle, Kobayashi (1972c)         |                                                  |
| Methane—ethane—propane                                    | 115–143              | 1                   | Watanabe, Kuroki, Oguro Saito (1969) | Graphs only                                      |
| Methane—ethane— <i>n</i> -butane                          | —                    | —                   | Cota, Thodos (1962)                  | Measurement of critical temperature and pressure |
| Methane—propane— <i>n</i> -butane                         | 311                  | 48–117              | Rigas, Mason, Thodos (1959)          |                                                  |
| Methane—propane— <i>n</i> -butane                         | 278–378              | 0–100               | Wiese, Jacobs, Sage (1970)           |                                                  |
| Ethyne—ethene—ethane                                      | 236, 255, 278        | 10–32               | Hogan, Nelson, Hanson, Cines (1955)  |                                                  |
| Ethyne—ethene—ethane                                      | 278, 289             | 32–52               | McCurdy, Katz (1944)                 |                                                  |
| Hydrogen—carbon monoxide—nitrogen—oxygen—methane          | 78, 90               | 6–78                | Torochnesnikov, Gurevich (1941)      |                                                  |
| Hydrogen—carbon monoxide—nitrogen—methane                 | —                    | —                   | Torochnesnikov, Serenova (1954)      |                                                  |
| Hydrogen—carbon monoxide—carbon dioxide—propane           | 273                  | 8–45                | Yorizane, Yoshimura, Masuoka (1972)  |                                                  |
| Hydrogen—carbon monoxide—carbon dioxide— <i>n</i> -butane | 273                  | 8–45                | Yorizane, Yoshimura, Masuoka (1972)  |                                                  |
| Hydrogen—nitrogen—methane—ethane                          | 144, 200             | 34, 68              | Cosway (1958), Cosway, Katz (1949)   |                                                  |
| Hydrogen—methane—ethene—ethane—propene—propane            | 200, 255             | 34, 68              | Benham (1956), Benham, Katz (1957)   |                                                  |

| System                                            | Temperature range, K | Pressure range, atm | Reference                     | Remarks     |
|---------------------------------------------------|----------------------|---------------------|-------------------------------|-------------|
| Helium—nitrogen—methane—ethane—propane—butane     | 123–183              | 7                   | Stutzman, Brown (1949)        |             |
| Nitrogen—methane—ethane—propane— <i>n</i> —butane | 153–253              | 28–38               | Banks, Haselden (1969)        |             |
| Methane—ethane—propane— <i>n</i> —butane          | 222                  | 14–20               | De Priester (1953)            |             |
| Methane—ethane—propane—isobutane                  | 244                  | 14                  | De Priester (1953)            |             |
| Natural gas system                                | 102–255              | 7–34                | Brandt, Stroud, Miller (1961) |             |
| Natural gas system                                | 229–300              | 34, 68, 101         | Buckley, Lightfoot (1941)     |             |
| Natural gas system                                | 311–411              | 34–204              | Roberts (1963)                |             |
| Natural gas system                                | 311–378              | 34–204              | Roberts, McKetta (1963)       |             |
| Natural gas system                                | 102–200              | 7–34                | Stroud, Miller, Brandt (1959) |             |
| Natural gas system                                | 339–394              | 7–136               | Stuckey (1966)                | Graphs only |

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## ERRATA

### LIQUID-VAPOUR EQUILIBRIA RESEARCH ON SYSTEMS OF INTEREST IN CRYOGENICS -- A SURVEY

by

A. J. Kidnay, M. J. Hiza, and R. C. Miller

in Cryogenics Vol. 13, No. 10, 575-99 (Oct. 1973)

- page 575: Last sentence of Abstract --- add CO<sub>2</sub> after CO.

- page 577: Change equations (7) and (10) as follows

$$\gamma_i = \gamma_i^{(R)} \frac{f_i^{o(R)}}{f_i^o} \exp \int_{\pi}^{\pi} (R) \frac{\bar{v}_i d\pi}{RT} \quad (7)$$

$$\bar{f}_j(\text{liquid}) = \gamma_j^* x_j H_{j,i} \quad (10)$$

- page 578: Ref. 4. Hala et al; change date to 1967.

- page 579: (a) - 4th entry under Hydrogen-helium 4; Roellig, Giese (1962); change remark to "Pressures given are partial pressures of helium"

(b) - 7th entry under Hydrogen-helium 4; Sonntag, Crain, Streett (1964); delete remark.

- page 581: 2nd entry under Hydrogen-methane; change Tikhovovich to Tikhonovich.

- page 583: Entry under Helium-krypton; change Kidney to Kidnay.

- page 586: 5th entry under Nitrogen-carbon dioxide; Muirbrook (1964), etc.; delete remark.

- page 588: 4th entry under Hydrogen sulphide-propane; Steckel (1945); change temperature from 237 to 273.
- page 591: Entry under Ethyne-propene; change reference date to (1945).
- page 592: After n-Butane-isobutane entries, insert new table title: "Liquid-vapour equilibria for ternary systems."
- page 594: After Ethyne-ethene-ethane entries, insert new table title: "Liquid-vapour equilibria for systems of four or more components."
- page 595: BIBLIOGRAPHY
  - (a) Abdulayev (1941); change Priki to Prikl
  - (b) Aerov et al. (1968); change Zalayaletoinova to Zalyaletoinova.
  - (c) Benham, Katz, Williams (1957); change AIChE J to AIChE J.
  - (d) Burn, Din (1962); change the page no. 1241 to 1341.
- page 596:
  - (a) Cines et al. (1953); add the page no. 1 ~ after (1953).
  - (b) Greene, Sonntag (1968); change )Plenum (Plenum.
  - (c) Hirata, Hakuta (1968); change the page no. 594 to 1594.
- page 597:
  - (a) Kulikov (1969); change the page no. 8 to 18.
  - (b) Morlet (1963); change the page no. 27 to 127.
  - (c) Newman, Jackson (1958); change the page no. 481 to 1481.



- page 598:
  - (a) Rodewald (1963); change An Arbor to Ann Arbor.
  - (b) Scheeline, Gilliland; change year and page no. from (1969) 69 to (1939) 1050.
- page 599:
  - (a) Watanabe et al. (1969); change the page no. 293 to 292.
  - (b) Yokoyama, Ohe (1971); add the page no. 4 after (1971).



## APPENDIX I

LIQUID-VAPOR EQUILIBRIA IN THE NITROGEN-METHANE  
SYSTEM BETWEEN 95 and 120 K

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Paper K-9  
Prepared for  
The 1973 Cryogenic Engineering Conference  
August 8, 9 and 10, 1973  
Georgia Institute of Technology  
Atlanta, Georgia

LIQUID-VAPOR EQUILIBRIA IN THE NITROGEN-METHANE  
SYSTEM BETWEEN 95 and 120 K\*

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ABSTRACT

A study was undertaken to obtain liquid-vapor equilibria data for the nitrogen-methane system at uniform temperature increments between the triple point of methane and the critical point of nitrogen. The measured liquid and vapor phase equilibria compositions and the derived excess Gibbs energy values for six isotherms from 95 to 120 K are compared with the corresponding values taken from other investigations. The excess Gibbs energy for the equimolar mixture exhibits a zero to slightly positive temperature dependence, in qualitative agreement with calculations based on the Snider-Herrington hard sphere model. This temperature dependence of the excess Gibbs energy also suggests that the excess enthalpy (heat of mixing) must be equal to or slightly less than the excess Gibbs energy.

INTRODUCTION

The development and evaluation of liquid mixture (solution) theory depends heavily on the availability of precise data for mixtures of simple molecules. The most useful data are for binary mixtures at closely spaced temperatures over as wide a temperature range as possible, both above and below the critical temperature of the most volatile component. The nitrogen-methane mixture, which is technologically important as one of the more important binary mixtures in liquefied natural gas, is an excellent compromise between theoretical and practical considerations.

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Key Words: Binary mixture, excess Gibbs energy, experimental phase equilibria data, heat of mixing, liquid-vapor equilibria, nitrogen-methane system.

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The interest in the phase equilibria properties of this particular system is apparent by the large number of studies reported in the literature. A number of experimental investigations have been conducted to determine the liquid-vapor equilibria properties of nitrogen-methane mixtures [1-15]. In addition, several investigations have been conducted to determine the solid-liquid equilibria and the three phase (solid-liquid-vapor) locus [16-19]. In the liquid-vapor region the data of Bloomer and Parent [1] and of Cines et al. [3] cover most of the methane liquid range, and consequently, one or the other of these data sets frequently has been used in correlations and for testing computation methods for the nitrogen-methane system [20-23]. Since the data of Bloomer and Parent are isobaric and those of Cines et al. are isothermal, direct comparisons are not possible. However, from comparisons made by Bloomer and Parent of isothermal crossplots of their data and those of Cines et al., these data sets appear to be in fairly good agreement at the lower temperatures, but are in less satisfactory agreement at the higher temperatures.

Of the remainder of the data reported prior to 1972, most studies were too limited to add independently to the description of the liquid-vapor equilibria behavior of this system. In addition, the method of investigation, i.e. isobaric dew-point, bubble-point measurements versus isothermal vapor-recirculation measurements, and the method of reporting data, i.e. graphical versus tabular, further complicate evaluation and comparison of all of the data.

The recent investigations of Miller et al. [10] at 112.00 K and of Stryjek et al. [13] from 113.72 K up to the methane critical temperature add new isothermal data which readily can be compared with some of the previous data sets. In the mutual liquid range of the two components, with which we are concerned in the present study, these newer data tend to highlight the discordant aspects of some of the previous data more clearly.

In addition to phase equilibria data, density or more specifically excess molar volumes are vital to the development of liquid mixture theory. Liu and Miller [24] recently reported excess molar volumes for the nitrogen-methane system between 90 and 120 K. Subsequently, Massengill and Miller [25] provided an interesting theoretical discussion of the effects of adjustments to the combining rules and of predictions of excess molar volume and excess Gibbs energy as a function of temperature with a modified hard sphere equation of state. Because of the lack of consistency of phase equilibria data for the nitrogen-methane system in the same temperature region, it is difficult to draw definitive conclusions from their treatise. Thus, the need for a consistent set of phase equilibria data for the nitrogen-methane system between 90 and 120 K was clearly indicated.

The purpose of the present study was to obtain liquid-vapor equilibria data for the nitrogen-methane system at 5 K increments of temperature between the triple point of methane and the critical point of nitrogen, and from these data to obtain the magnitude and temperature dependence of the excess Gibbs energy. These values of excess Gibbs energy provide the basis of comparison with the corresponding values derived from other data and with the qualitative temperature dependence of the excess Gibbs energy predicted from the hard sphere model by Massengill and Miller [25].

## EXPERIMENTAL

The liquid-vapor equilibria measurements were made in a closed-loop vapor-recirculating system described previously [26]. Thus, other than some minor differences, discussion of experimental details need not be included here.

The equilibrium pressures were measured with a standard laboratory, double-revolution, 0-20 bar Bourdon gage and a 0-100 psia spiral quartz Bourdon gage. The 20 bar gage has a claimed accuracy of  $\pm 0.1\%$  of full

scale and was found to be consistently better than these limits when compared with the 100 psia gage. The latter instrument was calibrated against an air dead-weight gage in this laboratory giving a maximum uncertainty of less than  $\pm 0.1$  psia over the full range. The pressure tap was a small tube connected directly to the top of the equilibrium cell and was independent of the recirculation system.

Temperatures were controlled as described previously [26]. However, the reported temperatures are those determined by vapor pressure measurements of pure methane and pure nitrogen as compared with the new methane data of Prydz and Goodwin [27] and the nitrogen values from the equation of Strobridge [28]. For our purposes, nitrogen vapor pressure values from the equation of Strobridge are in excellent agreement with the newer data of Weber [29]. Within experimental uncertainties of the present study, the temperatures reported here are consistent with the IPTS-68 temperature scale.

Compositions were determined chromatographically with helium elution gas and thermal conductivity detector. Calibration gas mixtures were prepared on a pressure basis, corrected for nonideality, at 4.94, 9.90, and 49.89 mole % methane in nitrogen. These calibration mixtures and pure methane and pure nitrogen were analyzed at a number of different sample pressures to determine analyzer response as a function of component partial pressure. It was determined that a linear calibration based on the pure species at near atmospheric pressure (60 cm Hg) satisfactorily reproduced compositions over the entire composition range of interest, based on peak areas, within 0.5% of the actual composition of the minor component. Since this difference is approximately equivalent to the precision of analysis, the results reported here are based entirely on pure component calibrations. The experimental liquid and vapor compositions are thought to be accurate within  $\pm 1\%$  of the actual composition or within  $\pm 0.1$  mole %, whichever is greater.

Liquid samples were withdrawn directly from the bottom of the equilibrium cell through a stainless steel capillary tube, while the vapor samples were isolated in a room temperature sample loop which included the pump free volume. In all cases, compositions were determined by analysis of both components in the mixture. The total sample pressure was taken as the sum of the partial pressures determined in the analysis. Though total sample pressure was measured, the sum of the partial pressures was used to compensate for slight variations in analyzer sensitivity and for any lack of sample thermal equilibrium.

It is also worth noting that the apparatus and chromatograph used in this study were the same as those used in the study of Miller et al. [10]. However, there were significant differences. The more precise 100 psia quartz Bourdon gage was acquired for the present study to improve the measurement of the lower pressures. The standard mixtures, except the pure component species, were prepared separately for each study using different methods. The calibration mixtures used in the earlier study were only equimolar mixtures prepared by weight. However, it was determined in both studies that assuming linear response based on calibration of the chromatograph with the pure fluid species represented the compositions of the prepared standard mixtures within the precision of analysis. In addition, temperatures reported in the earlier study were taken from the platinum thermometer readings, while in the present study the control point and thus the experimental temperature were determined by the vapor pressures of the pure component species. Thus, the two investigations are significantly different to be considered as two independent investigations.

## RESULTS AND DISCUSSION

Equilibrium liquid and vapor compositions were measured at 95.00, 100.00, 105.00, 110.00, 115.00, and 120.00 K. The results of these measurements, along with the vapor pressures of the pure components, are given in Table 1.

A negative departure from Raoult's law occurs on the nitrogen rich end at the higher temperatures, consistent with the data of Bloomer and Parent [1], Cines et al. [3], Stryjek et al. [13], and Miller et al. [10]. However, the isotherm of Chang and Lu [4] at 122.05 K does not show this negative departure. Extrapolation of the data of Chang and Lu to the pure nitrogen axis suggests a higher nitrogen vapor pressure than that for 122 K and thus a slightly higher temperature than that reported, which could easily account for the discrepancy.

In figure 1, the liquid and vapor phase compositions at 100.00 K from the present investigation are compared with the smoothed values of Cines, et al. [3] at 99.82 K. This is the only direct comparison that can be made with the experimental data of other investigators. The significant point worth noting is that, even though the data of Cines et al. are for a slightly lower temperature, their vapor phase compositions are lower in nitrogen content than the present data. From the temperature dependence of the vapor phase compositions of the present study, the nitrogen content should be higher at the lower temperature. This is significant since the activity coefficient of methane is strongly affected by this inconsistency.

A sensitive method for comparing close-boiling liquid-vapor equilibria data is through the derived excess Gibbs energy,  $G^E$ , as a function of temperature and composition. This topic was discussed in some detail in an earlier paper by Duncan and Hiza [30]. The composition dependence of  $G^E$  is obtained from

$$G^E = x_1 RT \ln \gamma_1 + x_2 RT \ln \gamma_2 \quad (1)$$

where  $x$  is the liquid phase mole fraction and  $\gamma$  is the activity coefficient. The equation selected here for calculating the activity coefficient for each component is the one given in reference 30 and will not be repeated here. This equation is based on the virial equation of state and includes third virial coefficient effects. The activity coefficients thus calculated are corrected to a reference pressure, which for our purposes has been taken as one bar.



Second virial coefficients for pure nitrogen and the interaction second virial coefficients for nitrogen-methane were calculated from the corresponding states equation of McGlashan and Potter [31]. The mixture characteristic temperature was calculated from

$$T_{c12} = (1 - k_{12}) (T_{c1} T_{c2})^{1/2} \quad (2)$$

in which the value of  $k_{12}$  of 0.03 was taken. The characteristic volume of the mixture was calculated from the arithmetic mean rule

$$V_{c12} = 1/8 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \quad (3)$$

For pure methane, second virial coefficients were taken from Goodwin [32]. Molar volumes for pure liquid methane and for pure liquid nitrogen were taken from Goodwin and Prydz [33] and from Strobridge [28], respectively. Isothermal compressibility for the pure liquids were taken from Rowlinson [34]. For purposes of the present calculations, it was assumed that the molar volume and compressibility of each component in the mixture are the same as those of the pure fluid.

Values of the equimolar  $G^E$  for much of the previous data on the nitrogen-methane system are shown in figure 2. The values given include those obtained using both experimental liquid and vapor phase data (filled symbols) and those obtained from the liquid phase data only by the method attributed to Barker [35]. In both methods, the derived values of  $G^E$  were fitted by the method of least squares to the following equation

$$G^E = x_1 x_2 RT [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (4)$$

where 1 refers to nitrogen. The values shown in figure 2 were calculated from the fit of equation (4) obtained by each method. The two values shown for Fastovskii and Petrovskii [6], however, were calculated from the smoothed equimolar liquid and vapor compositions tabulated in their paper, interpolated from the original isobaric data.

The curve shown in figure 2 was calculated by Massengill [36] from the hard sphere model applied by Snider and Herrington [37]. This curve was adjusted by Massengill to fit approximately the equimolar  $G^E$  value of Miller et al. [10] at 112.00 K by including a  $k_{12}$  correction for the "a" parameter of 0.035, similar to the correction indicated in equation (2).

Though values of  $G^E$  obtained from the two methods are not expected to be exactly equal, the results from both methods should exhibit the same temperature dependence if the data were internally and mutually consistent. It is not possible to conclude from the data presented in figure 2 that the temperature dependence of the excess Gibbs energy predicted from the hard sphere model is either reasonable or incorrect.

The values of  $G^E$  calculated from the present liquid and vapor phase data are given in Table 1 also. The constants of equation (4) obtained from these values and from the Barker method are given in Table 2. The equimolar  $G^E$  values from both methods are compared in figure 3 with those from the previous data of Miller et al. [10] and the calculated curve taken from Massengill [36]. The values of the equimolar  $G^E$  from the present study are in excellent agreement with those from Miller et al. Furthermore, the results obtained from both methods give the same temperature dependence, though the absolute values differ by about 10%. It thus can be concluded that the calculated curve is a reasonable representation of the temperature dependence of  $G^E$ .

The fact that the heat of mixing,  $H^E$ , is related to the excess Gibbs energy and its temperature dependence by

$$H^E = G^E - T(\partial G^E / \partial T)_P \quad (5)$$

also allows a conclusion about the heat of mixing for this system. From approximately 90 to 110 K, the value of  $G^E$  remains essentially constant. Thus, the temperature dependence is zero and  $H^E$  and  $G^E$  are equal. Above 110 K the temperature dependence becomes slightly positive; thus, the value of  $H^E$  would become less than the value of  $G^E$  in this region. Unfortunately, there are no calorimetric heat of mixing data for this system to substantiate this deduction.

Additional comparisons are given in figures 4, 5, and 6 between the isothermal  $G^E$  values from the liquid and vapor phase data of the present study at 95.00, 115.00, and 120.00 K and the corresponding values from four other investigations at approximately the same temperatures. It is apparent that the  $G^E$  values from the present study are more symmetrical about the equimolar value than those from the other investigations. The values from Stryjek et al. and Cines et al. are in reasonably good agreement with the present results at these temperatures. Those from Sprow and Prausnitz, however, are significantly lower than the present results. With the exception of two points, the  $G^E$  values from the data of Chang and Lu are in reasonable agreement with values from the present study, which is surprising considering the qualitative difference apparent in their data in the nitrogen rich end.

#### SUMMARY

The results of this investigation provide a single set of closely spaced and consistent liquid-vapor equilibria data for the nitrogen-methane system between the triple point temperature of methane and the critical point of nitrogen. The derived excess Gibbs energy values substantiate the qualitative temperature dependence of the equimolar Gibbs energy predicted by the hard sphere model of Snider and Herrington as applied by Massengill. From the temperature dependence of the excess Gibbs energy, it can be concluded that the nitrogen-methane system closely approximates a regular solution over much of the temperature range examined, i.e.  $H^E = G^E$  and  $S^E = 0$ . These conclusions strongly suggest the desirability of calorimetric heat of mixing measurements for the nitrogen-methane system, at least in the lower temperature region of this investigation.

#### ACKNOWLEDGEMENTS

The authors wish to express their thanks to R. C. Miller for providing the calculated values of the equimolar Gibbs energy, given only graphically in the thesis of one of his students, D. R. Massengill.

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TABLE 1. Experimental nitrogen-methane liquid-vapor equilibria properties.

| T, K   | $x_{N_2}$ | P, bars | $y_{N_2}$ | $\gamma_{N_2}$ | $\gamma_{CH_4}$ | $G^E$ , J/mol |
|--------|-----------|---------|-----------|----------------|-----------------|---------------|
| 95.00  | 0.0000    | 0.199   | 0.0000    |                |                 |               |
|        | 0.2679    | 2.254   | 0.9216    | 1.5755         | 1.0950          | 148.67        |
|        | 0.3562    | 2.737   | 0.9374    | 1.4433         | 1.1790          | 186.99        |
|        | 0.4249    | 3.018   | 0.9460    | 1.3355         | 1.2384          | 194.24        |
|        | 0.5271    | 3.431   | 0.9573    | 1.2238         | 1.3271          | 189.77        |
|        | 0.5889    | 3.646   | 0.9618    | 1.1621         | 1.4361          | 187.42        |
|        | 0.7495    | 4.247   | 0.9756    | 1.0600         | 1.7038          | 139.92        |
|        | 0.8271    | 4.580   | 0.9823    | 1.0327         | 1.9007          | 108.73        |
|        | 1.0000    | 5.400   | 1.0000    |                |                 |               |
| 100.00 | 0.0000    | 0.343   | 0.0000    |                |                 |               |
|        | 0.1329    | 1.988   | 0.8336    | 1.8662         | 1.0275          | 88.48         |
|        | 0.2397    | 2.960   | 0.8907    | 1.6059         | 1.0987          | 153.91        |
|        | 0.3301    | 3.621   | 0.9168    | 1.4436         | 1.1286          | 168.15        |
|        | 0.3831    | 3.989   | 0.9277    | 1.3734         | 1.1547          | 174.87        |
|        | 0.4463    | 4.396   | 0.9372    | 1.2987         | 1.2099          | 184.71        |
|        | 0.5069    | 4.706   | 0.9448    | 1.2241         | 1.2614          | 180.44        |
|        | 0.5638    | 5.032   | 0.9508    | 1.1742         | 1.3398          | 181.37        |
|        | 0.6671    | 5.598   | 0.9618    | 1.1002         | 1.4799          | 161.46        |
|        | 0.8133    | 6.451   | 0.9764    | 1.0320         | 1.8111          | 113.52        |
|        | 1.0000    | 7.778   | 1.0000    |                |                 |               |
| 105.00 | 0.0000    | 0.565   | 0.0000    |                |                 |               |
|        | 0.2101    | 3.649   | 0.8533    | 1.6242         | 1.0605          | 129.47        |
|        | 0.2869    | 4.512   | 0.8855    | 1.4960         | 1.0963          | 158.15        |
|        | 0.4108    | 5.664   | 0.9149    | 1.3191         | 1.1835          | 186.00        |
|        | 0.4836    | 6.298   | 0.9275    | 1.2444         | 1.2478          | 192.13        |
|        | 0.6012    | 7.242   | 0.9440    | 1.1455         | 1.3831          | 184.21        |
|        | 0.7548    | 8.417   | 0.9626    | 1.0511         | 1.6684          | 142.43        |
|        | 0.8990    | 9.805   | 0.9829    | 1.0148         | 2.0457          | 74.64         |
|        | 1.0000    | 10.835  | 1.0000    |                |                 |               |

TABLE 1. (continued)

| T, K   | $x_{N_2}$ | P, bars | $y_{N_2}$ | $v_{N_2}$ | $CH_4$ | $G^E$ , J/mol |
|--------|-----------|---------|-----------|-----------|--------|---------------|
| 110.00 | 0.0000    | 0.844   | 0.0000    |           |        |               |
|        | 0.2093    | 4.810   | 0.8237    | 1.6008    | 1.0546 | 128.53        |
|        | 0.2856    | 5.916   | 0.8615    | 1.4743    | 1.0850 | 154.66        |
|        | 0.4061    | 7.450   | 0.8950    | 1.3129    | 1.1799 | 190.96        |
|        | 0.4843    | 8.366   | 0.9113    | 1.2342    | 1.2477 | 197.60        |
|        | 0.5008    | 8.479   | 0.9147    | 1.2112    | 1.2516 | 190.24        |
|        | 0.6056    | 9.603   | 0.9319    | 1.1278    | 1.3765 | 181.88        |
|        | 0.6948    | 10.580  | 0.9456    | 1.0756    | 1.5125 | 161.82        |
|        | 0.7956    | 11.797  | 0.9612    | 1.0364    | 1.7208 | 127.47        |
|        | 0.8978    | 13.179  | 0.9790    | 1.0131    | 1.9841 | 74.76         |
|        | 1.0000    | 14.680  | 1.0000    |           |        |               |
| 115.00 | 0.0000    | 1.327   | 0.0000    |           |        |               |
|        | 0.1891    | 5.882   | 0.7782    | 1.6384    | 1.0465 | 124.51        |
|        | 0.2868    | 7.725   | 0.8363    | 1.4712    | 1.0873 | 162.93        |
|        | 0.3989    | 9.580   | 0.8739    | 1.3218    | 1.1606 | 192.05        |
|        | 0.5027    | 11.130  | 0.8983    | 1.2148    | 1.2501 | 199.65        |
|        | 0.5789    | 12.218  | 0.9129    | 1.1515    | 1.3398 | 195.85        |
|        | 0.7110    | 14.170  | 0.9377    | 1.0736    | 1.5208 | 164.16        |
|        | 0.8043    | 15.650  | 0.9538    | 1.0344    | 1.7540 | 131.17        |
|        | 0.9040    | 17.474  | 0.9750    | 1.0116    | 2.0407 | 75.40         |
|        | 1.0000    | 19.389  | 1.0000    |           |        |               |
| 120.00 | 0.0000    | 1.919   | 0.0000    |           |        |               |
|        | 0.0977    | 4.984   | 0.6122    | 1.8083    | 1.0174 | 73.31         |
|        | 0.1938    | 7.549   | 0.7458    | 1.6058    | 1.0490 | 130.07        |
|        | 0.2990    | 9.982   | 0.8125    | 1.4348    | 1.0956 | 171.53        |
|        | 0.3978    | 12.100  | 0.8512    | 1.3177    | 1.1523 | 194.66        |
|        | 0.4959    | 13.942  | 0.8773    | 1.2136    | 1.2381 | 203.17        |
|        | 0.5938    | 15.919  | 0.9000    | 1.1444    | 1.3476 | 200.81        |
|        | 0.7055    | 18.029  | 0.9225    | 1.0748    | 1.5323 | 176.16        |
|        | 0.7877    | 19.880  | 0.9414    | 1.0459    | 1.6785 | 144.97        |
|        | 1.0000    | 25.128  | 1.0000    |           |        |               |

Table 2. Constants for equation (4) from the Barker method  
and from both liquid and vapor data.

| T<br>K | Data<br>Used | A        | Std Dev. A | B         | Std Dev. B | C         | Std Dev. C |
|--------|--------------|----------|------------|-----------|------------|-----------|------------|
| 95.00  | x-P          | 0.856566 | 0.018181   | 0.048882  | 0.026564   | -0.006273 | 0.030452   |
|        | x-y-P        | 0.989270 | 0.000249   | -0.039063 | 0.001553   | -0.060026 | 0.011018   |
| 100.00 | x-P          | 0.834333 | 0.004510   | 0.012843  | 0.006889   | 0.019011  | 0.011753   |
|        | x-y-P        | 0.883896 | 0.0001627  | -0.064193 | 0.001080   | 0.127218  | 0.005988   |
| 105.00 | x-P          | 0.797382 | 0.011029   | 0.036777  | 0.018664   | 0.028248  | 0.026115   |
|        | x-y-P        | 0.877361 | 0.000017   | 0.001976  | 0.000084   | 0.058049  | 0.000487   |
| 110.00 | x-P          | 0.769161 | 0.010578   | 0.024975  | 0.017310   | 0.017785  | 0.024585   |
|        | x-y-P        | 0.844515 | 0.000072   | 0.001095  | 0.000416   | 0.018386  | 0.002345   |
| 115.00 | x-P          | 0.773121 | 0.006625   | 0.030019  | 0.011782   | 0.045115  | 0.016687   |
|        | x-y-P        | 0.832951 | 0.000019   | 0.014834  | 0.000086   | 0.066556  | 0.000489   |
| 120.00 | x-P          | 0.753117 | 0.006021   | 0.048651  | 0.010289   | 0.058088  | 0.016019   |
|        | x-y-P        | 0.819650 | 0.000008   | 0.037988  | 0.000023   | 0.086550  | 0.000145   |

## LIST OF FIGURES

1. Liquid and vapor equilibrium compositions for the nitrogen-methane system at 100.00 K compared with those of Cines et al. (1953).
2. Values of equimolar  $G^E$  calculated from the literature data. The value shown for Fuks and Bellemans (1967) is their reported value.
3. Values of equimolar  $G^E$  from the data of this investigation compared with the values calculated from the data of Miller et al. (1973) at 112.00 K.
4. Values of  $G^E$  from the data at 95.00 K compared with the values calculated from the data of Sprow and Prausnitz (1967) at 90.67 K.
5. Values of  $G^E$  from the data at 115.00 K compared with the values calculated from the data of Stryjek et al. (1972) at 113.72 K.
6. Values of  $G^E$  from the data at 120.00 K compared with the values calculated from the data of Cines et al. (1953) and of Chang and Lu (1967) at 122.05 K.



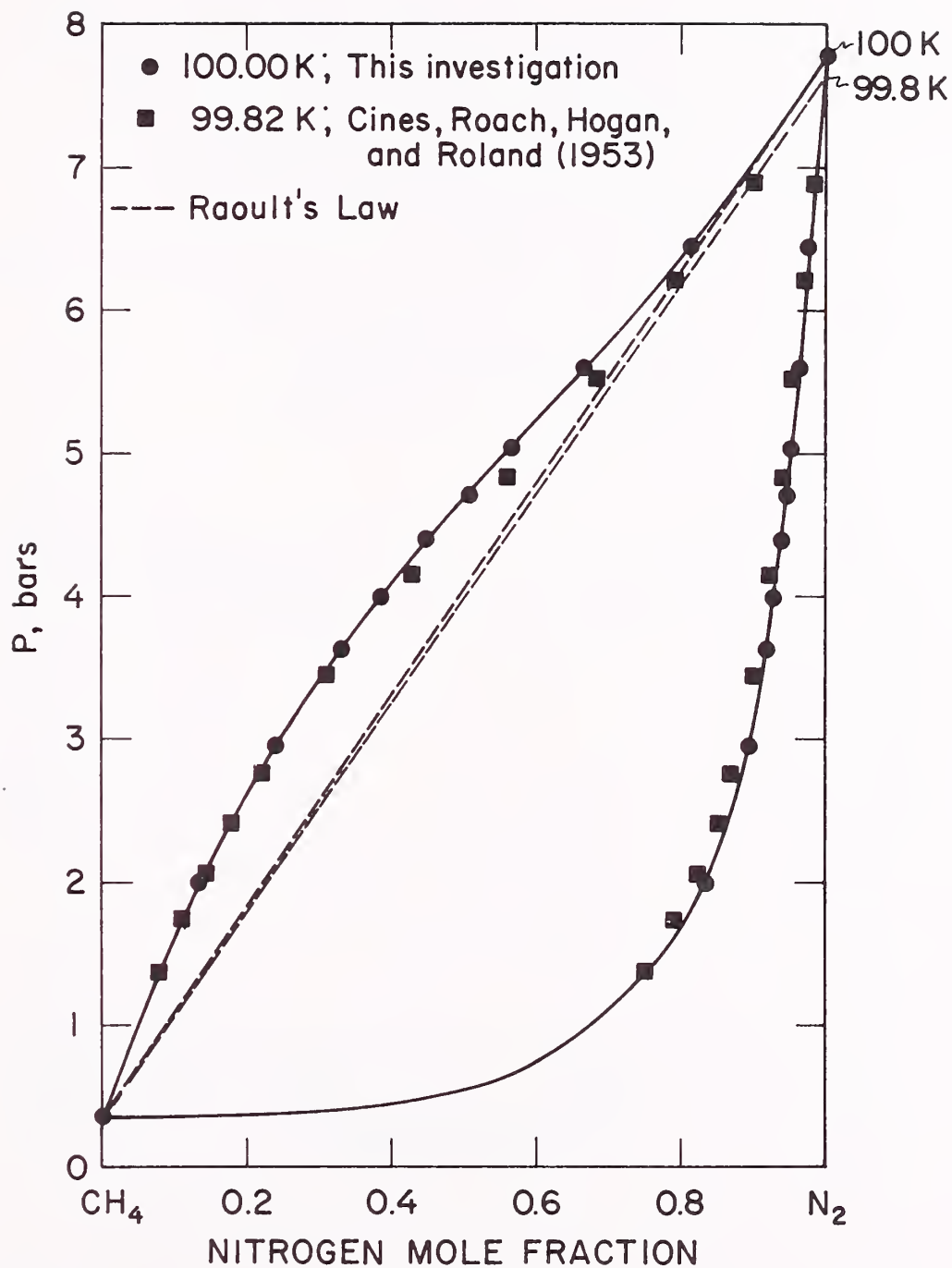


Figure 1.

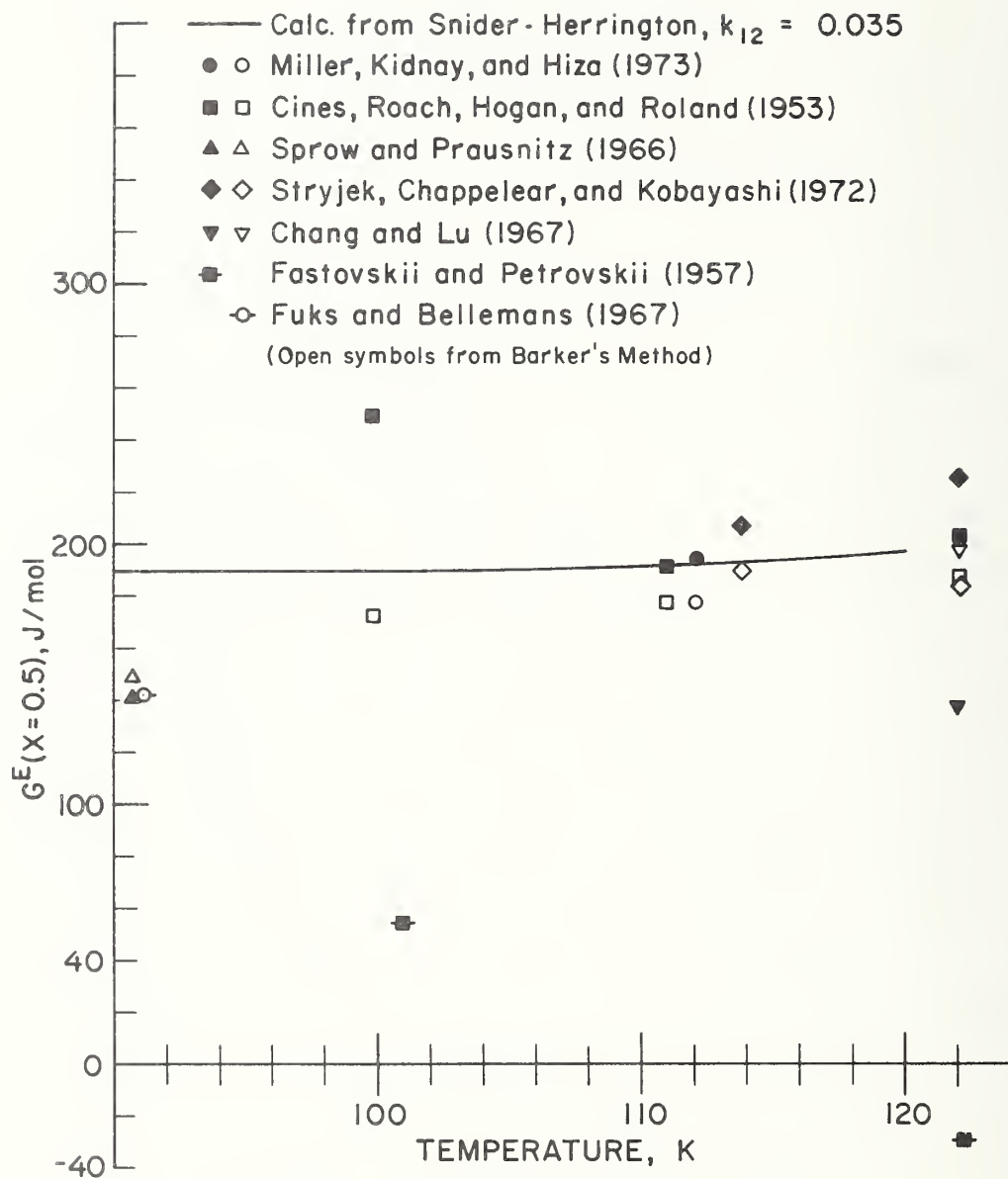


Figure 2.

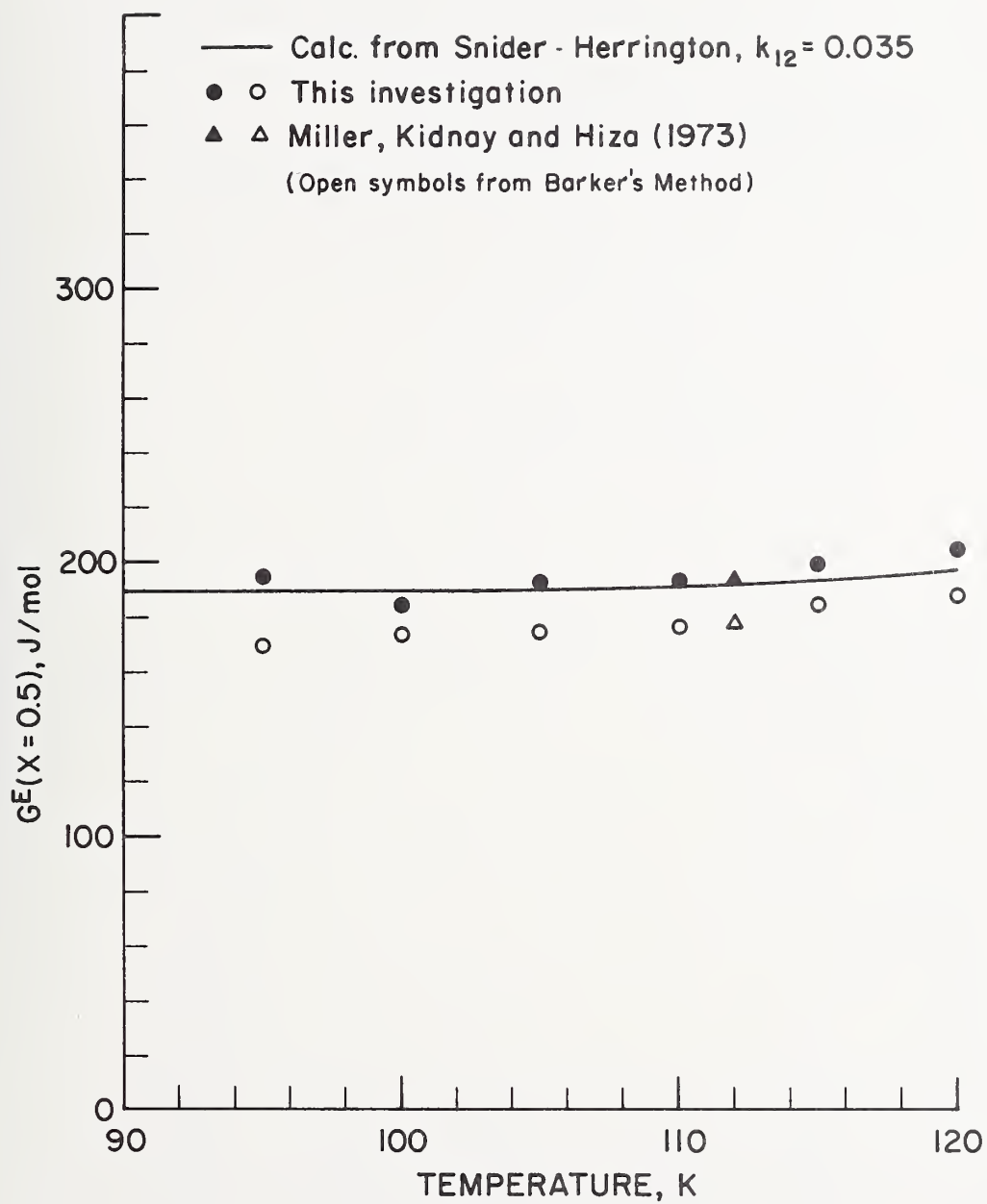


Figure 3.

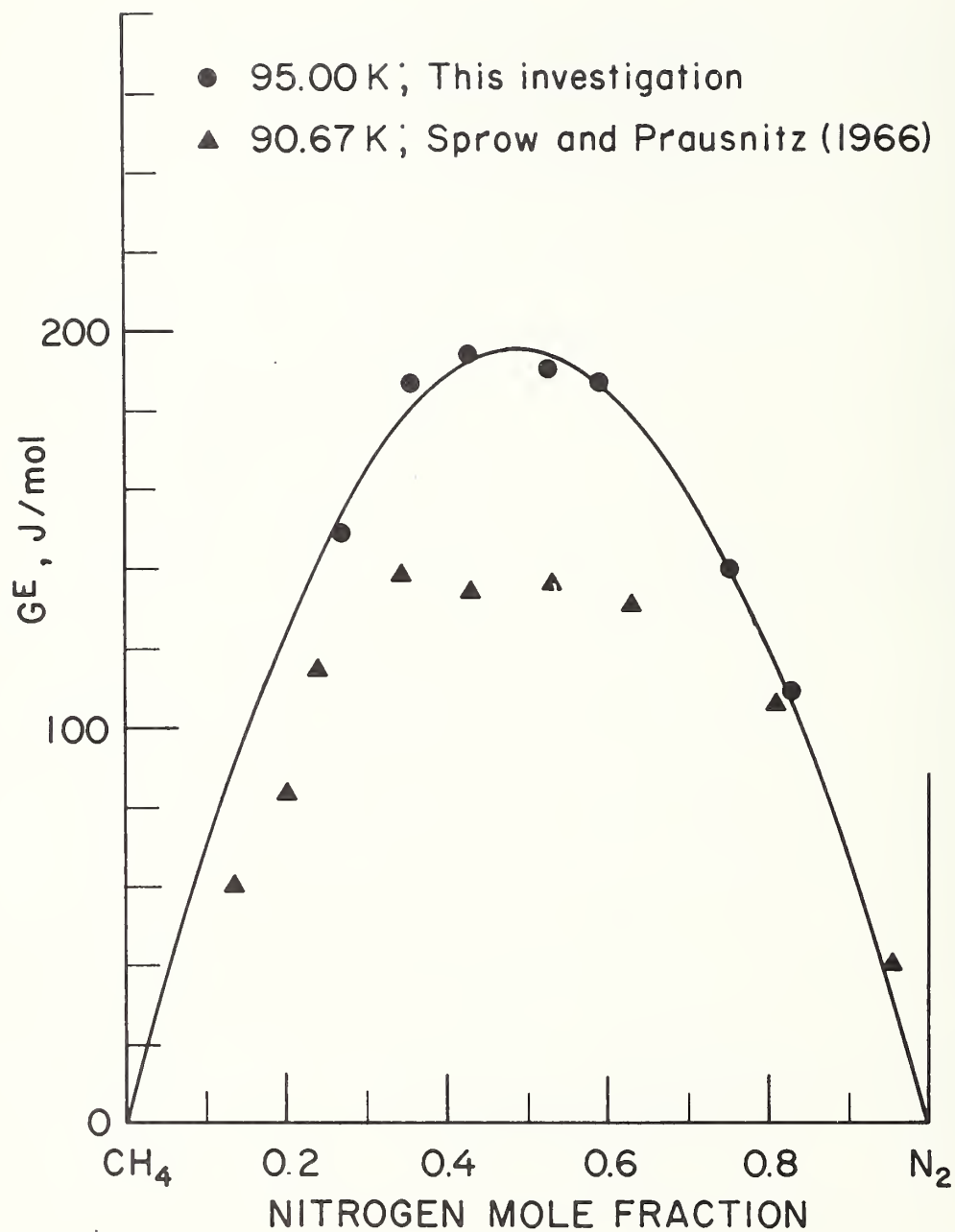


Figure 4.

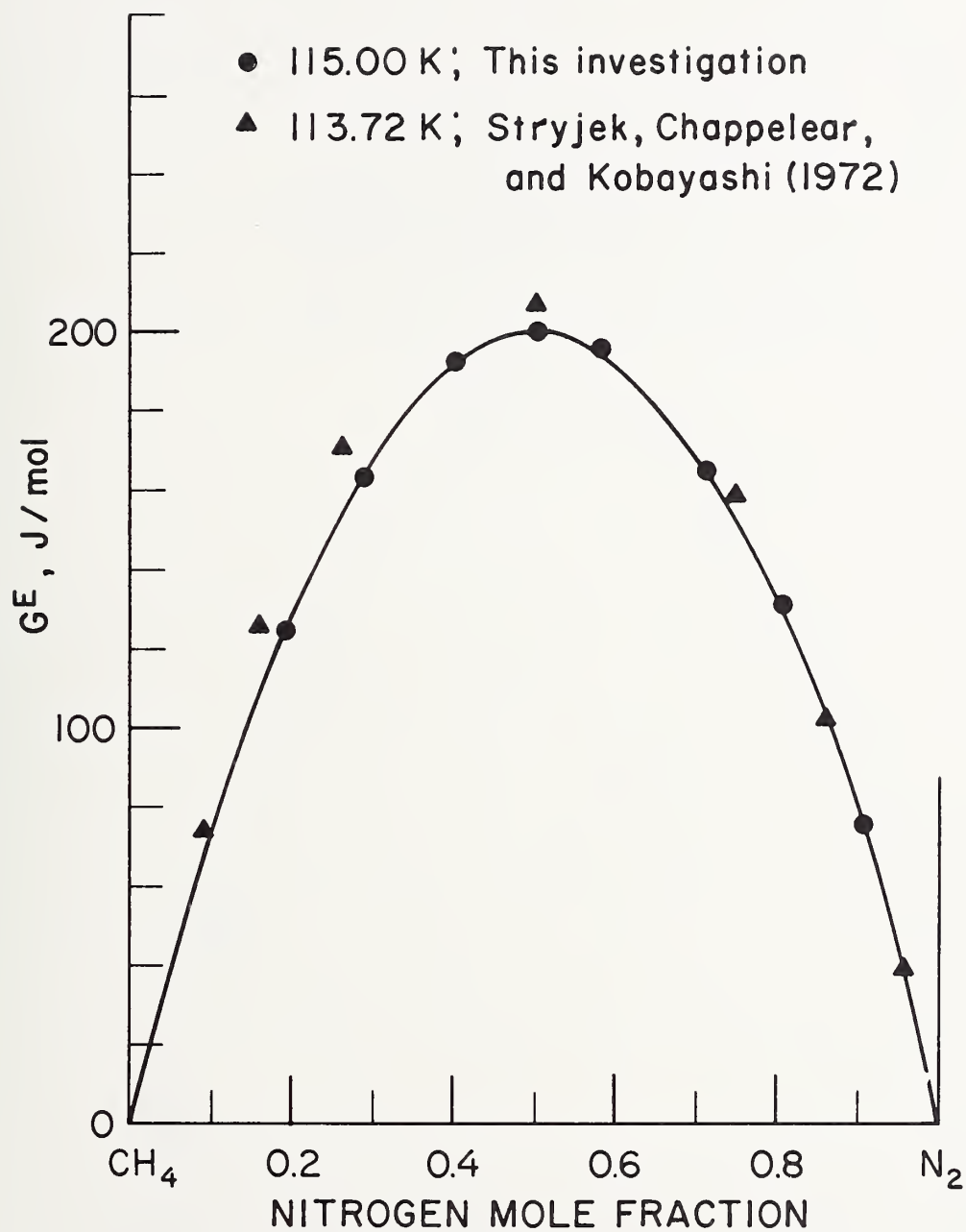


Figure 5.



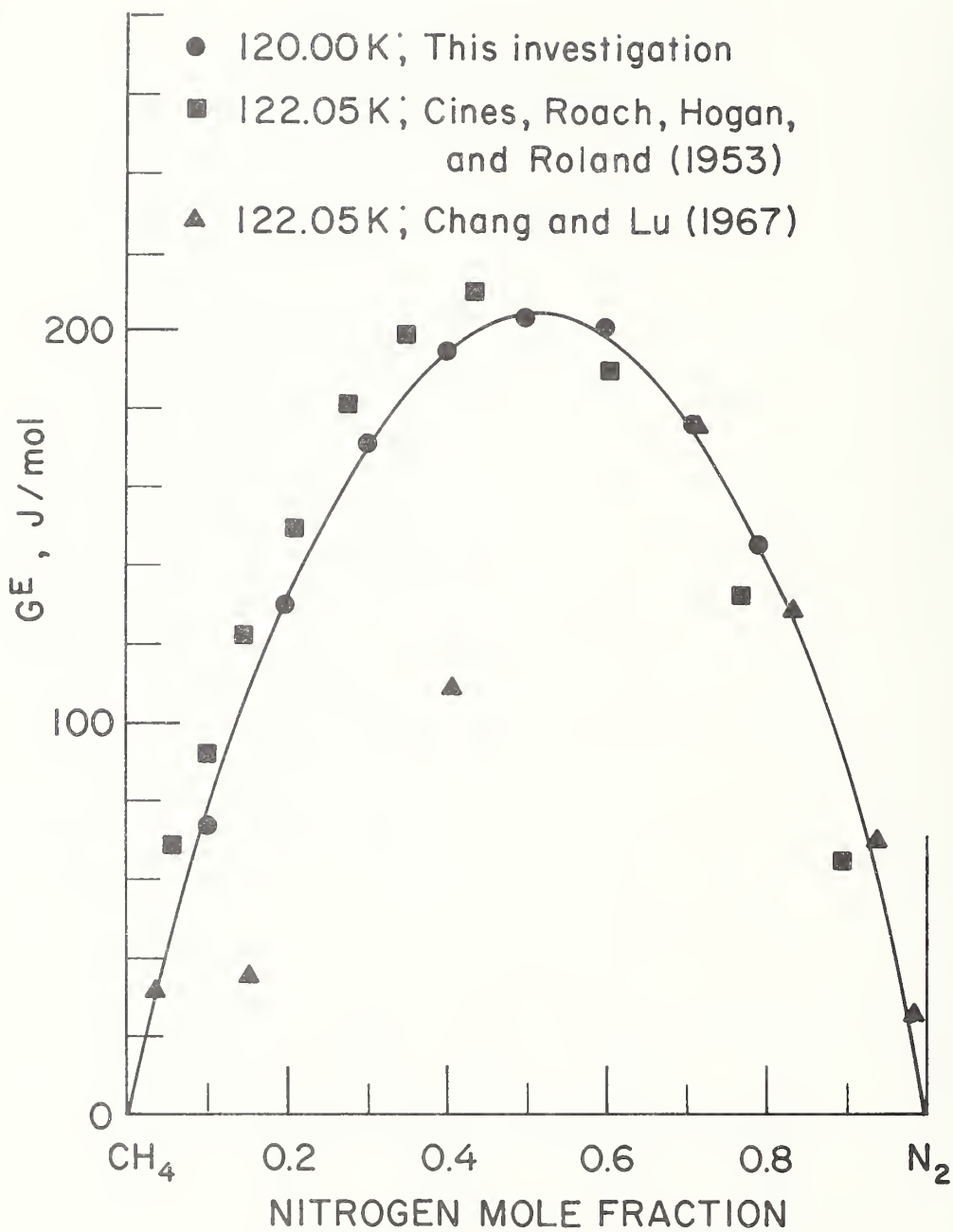


Figure 6.

## APPENDIX J

|                                                                                   |  |                                                   |                  |           |
|-----------------------------------------------------------------------------------|--|---------------------------------------------------|------------------|-----------|
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| SUBJECT<br><br>The Vapor Pressures of Ethane                                      |  | NAME<br>R. D. Goodwin<br><br>DATE<br>July 9, 1973 |                  |           |

This is the first of several reports planned on the physical properties of ethane. Our ultimate purpose is to compute tables of thermodynamic functions over the entire range of fluid states. We first will discover regions where data are inadequate or lacking by attempting to compute provisional tables based on existing data.

Accurate vapor pressures, and a proper analytical representation of these data, are essential for computing heats of vaporization via the Clapeyron equation.

In this note we give a limited bibliography. Not all of these references were available at this writing. We compare several sets of data by use of our new, non-analytic vapor pressure equation. We make a choice of the best for least squares, and we give deviations from this selected equation.

At the triple point near 90 K the vapor pressure of ethane is about 0.00001 atm (10  $\mu$ -atm). Experimental methods therefore differ for the range below one atm (184.5K) and for the range of higher pressures to 48 atm at  $T_c = 305$  K.

Data to about 1960 are reviewed by Tester [19], who selected the representation of Barkeley et al. [3] for the entire range from triple- to critical point.

Below one atm the data to 1964 are reviewed by Ziegler et al., who give their own, high quality set of data computed for thermodynamic consistency with all related or derived data, in a work for the National Standard Reference Data Program [23]. More recently we have the measurements of Carruth, obtained by the gas saturation flow technique, employing a flame ionization detector for analysis of the gas mixture [4]. See also J. J. Chen et al. (Rice University), paper G-1, 1972 Cryogenic Engineering Conference, on the same technique.

For high pressures the only new data of which we presently are aware are those of Pope (Table 25)[13], and those attributed to Dr. A. K. Pal by Pope [13] in Table 31. For these latter data there is no description of experimental method.

After this note was written we received the new precise measurements of Douslin and Harrison [24], and therefore have recomputed our results including these data. Douslin and Harrison note especially the new, precise measurements of Miniovich and Sorina [25], which were not available to us at this writing.

|                                                                                   |                               |                        |                                         |           |
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Our vapor pressure equation [6] uses the reduced argument,

$$x(T) \equiv (1-T_t/T)/(1-T_t/T_c),$$

where subscripts t and c refer to triple- and critical points,

$$\ln (P/P_t) = a \cdot x + b \cdot x^2 + c \cdot x^3 + d \cdot x^4 + e \cdot x \cdot (1-x)^\epsilon \quad (1)$$

and the exponent is  $\epsilon = 1.5$  for methane [15] and for oxygen [16]. Originally the term  $d \cdot x^4$  was absent. It has been added here to improve representation of the ethane data.

The following discoveries are found with the original equation of four terms. Optimum exponents in the range  $1.1 \leq \epsilon \leq 1.9$  are obtained merely by changing the sets of data used for least squares. Hence we must rely on the more precise methane and oxygen data to select  $\epsilon = 1.5$ . Varying the critical-point temperature within reasonable limits has no significant effect on the overall, rms relative pressure deviations.

By examining numerous results we have selected for least squares only the data of Ziegler at  $P \leq 1$  atm [23], and the data of Pope, Pal [13] and Douslin [24] at  $P > 1.9$  atm. Whereas the temperature scale of Ziegler may be thermodynamic (the report is not clear), we nevertheless find that deviations (rms in relative P) are minimized by converting both sets of data to T-1968 as if they had been on T-1948 [1]. All T used in the following are T-68.

The triple-point temperature was reviewed by Ziegler et al. Their selection of 89.89 K becomes 89.899 on the 1968 scale. The critical-point temperature 305.42 K of Pope has been changed to 305.33 K for consistency with the data of Douslin [24]. A value  $T_c = 305.33 \pm 0.005$  K is given by P. Sliwinski, Zeit. Phys. Chem. 68, 91 (1969) based on analysis of dielectric constants. This was kindly pointed out by D. E. Diller. We obtain pressures at these end points from the vapor pressure equation:

|                |             |                       |
|----------------|-------------|-----------------------|
|                | T, K (1968) | P, atm                |
| Triple point   | 89.899      | $9.616 \cdot 10^{-6}$ |
| Critical point | 305.33      | 48.07695              |

|                                                                                   |  |                        |                  |           |
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The constants for eq (1) were obtained via the data of Ziegler, Pope, Pal and Douslin. They include  $\epsilon = 1.6$  as shown at the head of table 1.

$$\begin{array}{ll}
 a = & 8.4549\ 8734 \qquad d = \quad -1.4138\ 6053 \\
 b = & 12.4880\ 3978 \qquad e = \quad \quad 8.5265\ 2253 \\
 c = & -4.1042\ 8155
 \end{array}$$

In the following tables we give the author's ID, his temperature and as converted to T-68, and the published and calculated pressures. Next is the deviation of his temperature from our calculated value,

$$DT \equiv T_{xpt} - T_{calc} = - (P_{xpt} - P_{calc}) / (dP/dT),$$

and finally his relative pressure deviation,

$$P, PCT \equiv 100 \cdot (P_{xpt} - P_{calc}) / P_{calc}.$$

At the bottom of each table we give the number of datum pairs, NP, and the rms of relative pressure deviations in percent.

The source of data in each table is identified by the numerical code, ID, in the first column--

| Table No. | I.D. | Authors                                  | Reference |
|-----------|------|------------------------------------------|-----------|
| 1         | 4    | A. K. Pal                                | [13]      |
|           | 7    | Ziegler et al.                           | [23]      |
|           | 9    | G. A. Pope                               | [13]      |
|           | 10   | Douslin, Harrison                        | [24]      |
| 2         | 1    | Tickner, Lossing                         | [20]      |
|           | 2    | API Proj. 44                             | [2]       |
|           | 3    | Carruth                                  | [4]       |
| 3         | 5    | Loomis, Walters                          | [11]      |
| 4         | 6    | F. Porter                                | [14]      |
|           | 8    | Barkelew et al                           | [3]       |
| 5         |      | Calculated vapor pressures (this report) |           |
| 6         |      | Reduced v.p. functions (this report)     |           |

|                                                                                   |                               |                                         |                  |           |
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As additional data may be found, we reserve comment on the deviations of individual authors, and omit the labor of preparing deviation plots.

Calculated pressures, slopes and curvatures are given at uniform temperatures by Table 5.

For comparison with functions in our original vapor pressure publication [6], we give these functions in Table 6, as computed via eq (1) namely

$$x(T) \equiv (T - T_t / T) / (1 - T_t / T_c),$$

$$Y(P) \equiv \ln(P / P_t) / \ln(P_c / P_t). \quad (2)$$

These variables range from zero to unity. The equation

$$Y = x \quad (3)$$

represents the basic vapor pressure equation

$$\ln(P) = a - b/T \quad (4)$$

when this is constrained to the end-points (triple and critical). Hence (Y-x) is the deviation of data from (4).

Finally, we give the computer programs used in this work as a means to check for errors, and to facilitate resumption of this research.

Addendum. Following work shows that the second virial coefficient used by Ziegler et al. to obtain vapor pressures is not consistent with our selection. At 200°K his  $B(T) = -455$  cc/mol, whereas our  $B(T) = -417.5$ . We therefore have recomputed our vapor pressure constants using Ziegler's vapor pressure data from his Table IX for "Curve B" of his Figure 1, for which  $B(T) = -410$  cc/mol at 200 K. The difference in his vapor pressures at 90 K is  $(7.80 - 7.33) / 7.33 = 6.4$  percent, the new values being the greater. Our new results for eq (1) are given in Table 7, (pages 20, 21) and tables 8, 9 on pages 22, 23 of this report. We prefer these constants for future use.



|                                                                                   |                               |                                                       |                  |           |
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|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | DATE<br>July 9, 1973   |                  |           |
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The Vapor Pressures of Ethane

Table 1. Data of Pal (4), Ziegler (7), Pope (9), and Douslin (10).

NAME

R. D. Goodwin

DATE

July 9, 1973

ETHANE VAPOR PRESSURES, E = 1.60

TTRP = 89.899, TCRT = 305.330

PTRP, MUATM = 9.61600, PCRT, ATM = 48.07695

8.454987344 12.488039775 -4.134281551

-1.413861533 8.526522526 0.000860000

| ID | T, XPTL | T-68    | P, ATM    | CALCD     | DEL T  | P, PCT |
|----|---------|---------|-----------|-----------|--------|--------|
| 7  | 94.000  | 94.013  | 0.0000274 | 0.0000274 | -0.001 | 0.02   |
| 7  | 98.000  | 98.012  | 0.0000693 | 0.0000694 | 0.002  | -0.05  |
| 7  | 102.000 | 102.008 | 0.0001618 | 0.0001619 | 0.002  | -0.05  |
| 7  | 106.000 | 106.002 | 0.0003526 | 0.0003522 | -0.006 | 0.11   |
| 7  | 110.000 | 109.998 | 0.0007207 | 0.0007205 | -0.002 | 0.03   |
| 7  | 114.000 | 113.995 | 0.0013947 | 0.0013947 | -0.000 | 0.00   |
| 7  | 118.000 | 117.991 | 0.0025697 | 0.0025698 | 0.000  | -0.00  |
| 7  | 122.000 | 121.988 | 0.0045303 | 0.0045293 | -0.002 | 0.02   |
| 7  | 126.000 | 125.987 | 0.0076737 | 0.0076734 | -0.000 | 0.00   |
| 7  | 130.000 | 129.987 | 0.012538  | 0.012540  | 0.001  | -0.01  |
| 7  | 134.000 | 133.988 | 0.019830  | 0.019834  | 0.002  | -0.02  |
| 7  | 138.000 | 137.990 | 0.030447  | 0.030460  | 0.004  | -0.04  |
| 7  | 142.000 | 141.993 | 0.045504  | 0.045527  | 0.005  | -0.05  |
| 7  | 146.000 | 145.996 | 0.066355  | 0.066389  | 0.006  | -0.05  |
| 7  | 150.000 | 150.000 | 0.094508  | 0.094657  | 0.006  | -0.05  |
| 7  | 154.000 | 154.004 | 0.13213   | 0.13220   | 0.007  | -0.05  |
| 7  | 158.000 | 158.008 | 0.18109   | 0.18117   | 0.005  | -0.04  |
| 7  | 162.000 | 162.012 | 0.24392   | 0.24397   | 0.003  | -0.02  |
| 7  | 166.000 | 166.015 | 0.32333   | 0.32330   | -0.001 | 0.01   |
| 7  | 170.000 | 170.019 | 0.42230   | 0.42214   | -0.006 | 0.04   |
| 7  | 174.000 | 174.023 | 0.54409   | 0.54371   | -0.011 | 0.07   |
| 7  | 178.000 | 178.026 | 0.69224   | 0.69145   | -0.020 | 0.11   |
| 7  | 182.000 | 182.028 | 0.87047   | 0.86905   | -0.029 | 0.16   |
| 7  | 184.520 | 184.550 | 1.00100   | 0.99803   | -0.036 | 0.20   |
| 9  | 198.181 | 198.216 | 1.9737    | 1.9758    | 0.023  | -0.11  |
| 4  | 214.302 | 214.334 | 3.9209    | 3.9176    | -0.021 | 0.08   |
| 4  | 224.102 | 224.130 | 5.6367    | 5.6429    | 0.031  | -0.11  |
| 4  | 229.756 | 229.782 | 6.8569    | 6.8629    | 0.026  | -0.09  |
| 4  | 234.558 | 234.581 | 8.0335    | 8.0423    | 0.034  | -0.11  |
| 9  | 234.692 | 234.715 | 8.0741    | 8.0772    | 0.012  | -0.04  |
| 10 | 238.150 | 238.150 | 9.0097    | 9.0108    | 0.004  | -0.01  |
| 9  | 238.771 | 238.792 | 9.1843    | 9.1935    | 0.032  | -0.10  |
| 4  | 239.844 | 239.864 | 9.4959    | 9.5049    | 0.030  | -0.09  |
| 4  | 240.514 | 240.534 | 9.6960    | 9.7032    | 0.024  | -0.07  |
| 10 | 243.150 | 243.150 | 10.5063   | 10.5071   | 0.003  | -0.01  |
| 4  | 243.559 | 243.577 | 10.5760   | 10.5790   | 0.009  | -0.03  |
| 4  | 246.814 | 246.830 | 11.7137   | 11.7183   | 0.014  | -0.04  |
| 4  | 247.816 | 247.831 | 12.0502   | 12.0648   | 0.042  | -0.12  |
| 10 | 248.150 | 248.150 | 12.1756   | 12.1766   | 0.003  | -0.01  |
| 4  | 249.741 | 249.755 | 12.7520   | 12.7512   | -0.030 | 0.08   |
| 4  | 250.146 | 250.160 | 12.8985   | 12.8991   | 0.002  | -0.01  |
| 4  | 251.587 | 251.600 | 13.4425   | 13.4356   | -0.018 | 0.05   |
| 4  | 252.544 | 252.556 | 13.8065   | 13.8008   | -0.015 | 0.04   |
| 10 | 253.150 | 253.150 | 14.0310   | 14.0310   | -0.000 | 0.00   |
| 4  | 254.290 | 254.301 | 14.4898   | 14.4854   | -0.011 | 0.03   |
| 4  | 257.543 | 257.552 | 15.8252   | 15.8264   | 0.003  | -0.01  |
| 10 | 258.150 | 258.150 | 16.0835   | 16.0823   | -0.003 | 0.01   |

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|---------------------------------------------------------|---------|---------|---------|---------|-------------|---------------|------|
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| Table 1--continued.                                     |         |         |         |         | DATE        | July 9, 1973  |      |
| ID                                                      | T, XPTL | T-68    | P, ATM  | CALCD   | DEL T       | P, PCT        |      |
| 10                                                      | 263.150 | 263.150 | 18.3464 | 18.3433 | -0.007      | 0.02          |      |
| 4                                                       | 263.380 | 263.386 | 18.4543 | 18.4553 | 0.002       | -0.01         |      |
| 4                                                       | 267.536 | 267.539 | 20.5197 | 20.5113 | -0.016      | 0.04          |      |
| 10                                                      | 268.150 | 268.150 | 20.8318 | 20.8274 | -0.009      | 0.02          |      |
| 4                                                       | 271.749 | 271.750 | 22.7661 | 22.7618 | -0.008      | 0.02          |      |
| 9                                                       | 272.949 | 272.949 | 23.4515 | 23.4347 | -0.030      | 0.07          |      |
| 10                                                      | 273.150 | 273.150 | 23.5549 | 23.5488 | -0.011      | 0.03          |      |
| 4                                                       | 275.922 | 275.921 | 25.1584 | 25.1648 | 0.011       | -0.03         |      |
| 4                                                       | 276.363 | 276.362 | 25.4558 | 25.4293 | -0.044      | 0.10          |      |
| 4                                                       | 276.385 | 276.384 | 25.4491 | 25.4425 | -0.011      | 0.03          |      |
| 4                                                       | 276.514 | 276.513 | 25.5472 | 25.5203 | -0.044      | 0.11          |      |
| 4                                                       | 277.813 | 277.811 | 26.3185 | 26.3133 | -0.008      | 0.02          |      |
| 10                                                      | 278.150 | 278.150 | 26.5309 | 26.5233 | -0.012      | 0.03          |      |
| 4                                                       | 280.041 | 280.038 | 27.7139 | 27.7158 | 0.019       | -0.04         |      |
| 4                                                       | 282.247 | 282.243 | 29.1537 | 29.1588 | 0.008       | -0.02         |      |
| 10                                                      | 283.150 | 283.150 | 29.7763 | 29.7681 | -0.012      | 0.03          |      |
| 4                                                       | 284.635 | 284.630 | 30.7664 | 30.7836 | 0.025       | -0.06         |      |
| 9                                                       | 284.845 | 284.840 | 30.9555 | 30.9296 | -0.037      | 0.08          |      |
| 4                                                       | 287.653 | 287.648 | 32.9289 | 32.9340 | 0.007       | -0.02         |      |
| 10                                                      | 288.150 | 288.150 | 33.3110 | 33.3030 | -0.011      | 0.02          |      |
| 4                                                       | 288.263 | 288.257 | 33.3899 | 33.3822 | -0.010      | 0.02          |      |
| 4                                                       | 290.040 | 290.034 | 34.6873 | 34.7148 | 0.036       | -0.08         |      |
| 9                                                       | 290.214 | 290.208 | 34.8748 | 34.8474 | -0.036      | 0.08          |      |
| 4                                                       | 292.236 | 292.229 | 36.4440 | 36.4182 | -0.033      | 0.07          |      |
| 4                                                       | 293.098 | 293.091 | 37.0816 | 37.1044 | 0.028       | -0.06         |      |
| 10                                                      | 293.150 | 293.150 | 37.1583 | 37.1518 | -0.008      | 0.02          |      |
| 9                                                       | 293.266 | 293.259 | 37.2672 | 37.2394 | -0.035      | 0.07          |      |
| 4                                                       | 296.347 | 296.339 | 39.7598 | 39.7842 | 0.029       | -0.06         |      |
| 10                                                      | 298.150 | 298.150 | 41.3494 | 41.3450 | -0.005      | 0.01          |      |
| 4                                                       | 299.065 | 299.057 | 42.6543 | 42.6822 | 0.031       | -0.07         |      |
| 9                                                       | 299.863 | 299.855 | 42.8863 | 42.8606 | -0.028      | 0.06          |      |
| 4                                                       | 300.205 | 300.196 | 43.1650 | 43.1703 | 0.006       | -0.01         |      |
| 4                                                       | 301.251 | 301.242 | 44.1085 | 44.1297 | 0.023       | -0.05         |      |
| 10                                                      | 302.150 | 302.150 | 44.9809 | 44.9778 | -0.003      | 0.01          |      |
| 10                                                      | 303.150 | 303.150 | 45.9327 | 45.9295 | -0.003      | 0.01          |      |
| 4                                                       | 303.471 | 303.462 | 46.2032 | 46.2300 | 0.028       | -0.06         |      |
| 4                                                       | 303.477 | 303.468 | 46.2798 | 46.2358 | -0.046      | 0.10          |      |
| 9                                                       | 304.012 | 304.002 | 46.7736 | 46.7558 | -0.018      | 0.04          |      |
| 4                                                       | 304.049 | 304.039 | 46.7698 | 46.7920 | 0.023       | -0.05         |      |
| 10                                                      | 304.150 | 304.150 | 46.9040 | 46.9010 | -0.003      | 0.01          |      |
| 4                                                       | 304.360 | 304.350 | 47.0931 | 47.0974 | 0.004       | -0.01         |      |
| 4                                                       | 304.446 | 304.435 | 47.2198 | 47.1822 | -0.038      | 0.08          |      |
| 4                                                       | 304.519 | 304.508 | 47.2025 | 47.2544 | 0.052       | -0.11         |      |
| 4                                                       | 304.734 | 304.723 | 47.4310 | 47.4677 | 0.037       | -0.08         |      |
| 4                                                       | 304.796 | 304.785 | 47.5185 | 47.5294 | 0.011       | -0.02         |      |
| 4                                                       | 304.924 | 304.913 | 47.6846 | 47.6572 | -0.027      | 0.06          |      |
| 4                                                       | 304.960 | 304.969 | 47.7131 | 47.7132 | 0.000       | -0.00         |      |
| 4                                                       | 305.121 | 305.110 | 47.8496 | 47.8547 | 0.005       | -0.01         |      |
| 4                                                       | 305.135 | 305.124 | 47.8251 | 47.8688 | 0.043       | -0.09         |      |
| 10                                                      | 305.150 | 305.150 | 47.8992 | 47.8950 | -0.004      | 0.01          |      |
| 4                                                       | 305.153 | 305.142 | 47.8807 | 47.8869 | 0.006       | -0.01         |      |
| 10                                                      | 305.250 | 305.250 | 47.9994 | 47.9959 | -0.003      | 0.01          |      |

NP = 99, RMSPCT = 0.061



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Table 2. Data of Tickner (1), API (2), and Carruth (3).

NAME R. D. Goodwin

DATE July 9, 1973

| ID | T, XPTL | T-68    | P, ATM    | CALCD     | DEL T | P, PCT |
|----|---------|---------|-----------|-----------|-------|--------|
| 1  | 91.350  | 91.361  | 0.0000132 | 0.0000141 | 0.265 | -6.86  |
| 1  | 94.450  | 94.463  | 0.0000263 | 0.0000306 | 0.582 | -13.98 |
| 1  | 98.550  | 98.562  | 0.0000658 | 0.0000783 | 0.730 | -15.98 |
| 1  | 101.850 | 101.858 | 0.0001316 | 0.0001571 | 0.797 | -16.23 |
| 1  | 105.350 | 105.353 | 0.0002632 | 0.0003118 | 0.825 | -15.60 |
| 1  | 110.550 | 110.548 | 0.0006579 | 0.0007914 | 0.992 | -16.87 |
| 1  | 114.650 | 114.644 | 0.0013158 | 0.0015453 | 0.947 | -14.85 |
| 1  | 119.050 | 119.040 | 0.0026316 | 0.0029942 | 0.839 | -12.11 |
| 1  | 125.550 | 125.537 | 0.0065789 | 0.0072450 | 0.717 | -9.19  |
| 1  | 130.650 | 130.637 | 0.013158  | 0.013539  | 0.240 | -2.81  |

NP = 10, RMSPCT = 13.226

| ID | T, XPTL | T-68    | P, ATM   | CALCD    | DEL T  | P, PCT |
|----|---------|---------|----------|----------|--------|--------|
| 2  | 130.270 | 130.257 | 0.013158 | 0.012947 | -0.138 | 1.63   |
| 2  | 136.460 | 136.449 | 0.026316 | 0.025909 | -0.148 | 1.57   |
| 2  | 140.410 | 140.402 | 0.039474 | 0.038925 | -0.141 | 1.41   |
| 2  | 143.370 | 143.364 | 0.052632 | 0.051945 | -0.139 | 1.32   |
| 2  | 145.760 | 145.756 | 0.065789 | 0.064946 | -0.142 | 1.30   |
| 2  | 147.790 | 147.788 | 0.078947 | 0.078018 | -0.134 | 1.19   |
| 2  | 151.120 | 151.121 | 0.10526  | 0.10415  | -0.127 | 1.07   |
| 2  | 153.820 | 153.824 | 0.13158  | 0.13028  | -0.122 | 0.99   |
| 2  | 159.030 | 159.039 | 0.19737  | 0.19591  | -0.099 | 0.74   |
| 2  | 162.960 | 162.973 | 0.26316  | 0.26140  | -0.094 | 0.67   |
| 2  | 166.170 | 166.185 | 0.32895  | 0.32708  | -0.084 | 0.57   |
| 2  | 168.900 | 168.918 | 0.39474  | 0.39284  | -0.074 | 0.48   |
| 2  | 173.410 | 173.432 | 0.52632  | 0.52422  | -0.064 | 0.40   |
| 2  | 177.100 | 177.125 | 0.65789  | 0.65574  | -0.056 | 0.33   |
| 2  | 180.250 | 180.277 | 0.78947  | 0.78743  | -0.046 | 0.26   |
| 2  | 183.010 | 183.039 | 0.92105  | 0.91908  | -0.039 | 0.21   |
| 2  | 184.520 | 184.550 | 1.00000  | 0.99803  | -0.036 | 0.20   |
| 2  | 185.480 | 185.510 | 1.0526   | 1.0509   | -0.031 | 0.16   |
| 2  | 187.710 | 187.741 | 1.1842   | 1.1821   | -0.034 | 0.18   |
| 2  | 189.770 | 189.802 | 1.3158   | 1.3143   | -0.023 | 0.11   |
| 2  | 193.440 | 193.473 | 1.5789   | 1.5777   | -0.017 | 0.08   |
| 2  | 198.150 | 198.185 | 1.9737   | 1.9729   | -0.008 | 0.04   |

NP = 22, RMSPCT = 1.857

| ID | T, XPTL | T-68    | P, ATM    | CALCD     | DEL T  | P, PCT |
|----|---------|---------|-----------|-----------|--------|--------|
| 3  | 91.340  | 91.351  | 0.0000152 | 0.0000141 | -0.315 | 8.14   |
| 3  | 93.700  | 93.712  | 0.0000270 | 0.0000255 | -0.237 | 5.80   |
| 3  | 96.240  | 96.253  | 0.0000491 | 0.0000466 | -0.235 | 5.42   |
| 3  | 100.700 | 100.710 | 0.0001297 | 0.0001239 | -0.222 | 4.64   |
| 3  | 105.600 | 105.603 | 0.0003263 | 0.0003268 | 0.009  | -0.16  |
| 3  | 114.240 | 114.235 | 0.0014461 | 0.0014487 | 0.012  | -0.19  |
| 3  | 120.380 | 120.369 | 0.0036066 | 0.0036185 | 0.023  | -0.33  |
| 3  | 129.810 | 129.797 | 0.012312  | 0.012260  | -0.036 | 0.42   |
| 3  | 135.770 | 135.759 | 0.024197  | 0.024065  | -0.051 | 0.55   |
| 3  | 140.550 | 140.542 | 0.040211  | 0.039472  | -0.188 | 1.87   |
| 3  | 144.140 | 144.135 | 0.056289  | 0.055871  | -0.080 | 0.75   |

NP = 11, RMSPCT = 3.759

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Table 3. Data (5) of Loomis, Walters [11].

NAME

R. D. Goodwin

DATE

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| ID | T, XPTL | T-68    | P, ATM   | CALCD    | DEL T  | P, PCT |
|----|---------|---------|----------|----------|--------|--------|
| 5  | 135.736 | 135.725 | 0.024500 | 0.023977 | -0.203 | 2.18   |
| 5  | 143.267 | 143.261 | 0.052200 | 0.051437 | -0.156 | 1.48   |
| 5  | 147.324 | 147.321 | 0.075900 | 0.074840 | -0.158 | 1.42   |
| 5  | 154.546 | 154.550 | 0.140000 | 0.13816  | -0.166 | 1.33   |
| 5  | 158.385 | 158.393 | 0.188600 | 0.18657  | -0.143 | 1.09   |
| 5  | 162.629 | 162.641 | 0.257300 | 0.25528  | -0.110 | 0.79   |
| 5  | 165.529 | 165.544 | 0.316000 | 0.31300  | -0.139 | 0.96   |
| 5  | 167.336 | 167.853 | 0.369300 | 0.36606  | -0.133 | 0.89   |
| 5  | 169.175 | 169.193 | 0.403300 | 0.40000  | -0.126 | 0.82   |
| 5  | 171.760 | 171.721 | 0.474300 | 0.47084  | -0.116 | 0.74   |
| 5  | 170.612 | 170.622 | 0.443000 | 0.43890  | -0.145 | 0.93   |
| 5  | 174.762 | 174.085 | 0.549800 | 0.54579  | -0.119 | 0.73   |
| 5  | 175.718 | 175.732 | 0.607300 | 0.60338  | -0.108 | 0.65   |
| 5  | 177.623 | 177.649 | 0.680400 | 0.67631  | -0.103 | 0.61   |
| 5  | 178.621 | 178.647 | 0.721000 | 0.71696  | -0.097 | 0.56   |
| 5  | 179.750 | 179.777 | 0.769600 | 0.76525  | -0.099 | 0.57   |
| 5  | 181.506 | 181.534 | 0.849900 | 0.84537  | -0.096 | 0.54   |
| 5  | 182.463 | 182.492 | 0.896300 | 0.89172  | -0.093 | 0.51   |
| 5  | 183.770 | 183.807 | 0.963400 | 0.95860  | -0.092 | 0.50   |
| 5  | 184.539 | 184.569 | 1.004000 | 0.99906  | -0.091 | 0.49   |
| 5  | 185.137 | 185.167 | 1.0366   | 1.0318   | -0.087 | 0.47   |
| 5  | 185.914 | 185.944 | 1.0800   | 1.0755   | -0.078 | 0.42   |
| 5  | 186.009 | 186.640 | 1.1206   | 1.1158   | -0.084 | 0.44   |
| 5  | 187.302 | 187.333 | 1.1619   | 1.1572   | -0.077 | 0.40   |
| 5  | 187.726 | 187.757 | 1.1881   | 1.1831   | -0.081 | 0.42   |
| 5  | 188.379 | 188.410 | 1.2289   | 1.2239   | -0.080 | 0.41   |
| 5  | 189.114 | 189.146 | 1.2757   | 1.2710   | -0.072 | 0.37   |
| 5  | 189.856 | 189.890 | 1.3248   | 1.3202   | -0.069 | 0.35   |
| 5  | 190.791 | 190.823 | 1.3885   | 1.3839   | -0.057 | 0.33   |
| 5  | 191.430 | 191.463 | 1.4334   | 1.4288   | -0.064 | 0.32   |
| 5  | 192.286 | 192.319 | 1.4953   | 1.4908   | -0.061 | 0.30   |
| 5  | 192.777 | 192.810 | 1.5318   | 1.5273   | -0.060 | 0.29   |
| 5  | 196.244 | 196.278 | 1.8088   | 1.8049   | -0.046 | 0.22   |
| 5  | 199.909 | 199.944 | 2.1417   | 2.1384   | -0.034 | 0.15   |

NP = 34, RMS PCT = 0.789



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Table 4. Data of Porter (6), and Barkelew (8).

NAME R. D. Goodwin  
DATE July 9, 1973

| ID | T,XPTL  | T-68    | P,ATM   | CALCD   | DEL T  | P,PCT |
|----|---------|---------|---------|---------|--------|-------|
| 6  | 184.470 | 184.500 | 0.99940 | 0.99534 | -0.075 | 0.41  |
| 6  | 203.490 | 203.524 | 2.4960  | 2.5076  | 0.106  | -0.46 |
| 6  | 205.620 | 205.653 | 2.7330  | 2.7489  | 0.135  | -0.58 |
| 6  | 210.960 | 210.992 | 3.4140  | 3.4308  | 0.121  | -0.49 |
| 6  | 216.310 | 216.341 | 4.2250  | 4.2338  | 0.054  | -0.21 |
| 6  | 221.880 | 221.910 | 5.2070  | 5.2104  | 0.018  | -0.06 |
| 6  | 225.100 | 225.128 | 5.8380  | 5.8456  | 0.037  | -0.13 |
| 6  | 226.180 | 226.207 | 6.0730  | 6.0709  | -0.010 | 0.03  |
| 6  | 234.580 | 234.603 | 8.0440  | 8.0481  | 0.016  | -0.05 |
| 6  | 238.900 | 238.921 | 9.2290  | 9.2305  | 0.005  | -0.02 |
| 6  | 243.220 | 243.238 | 10.5360 | 10.5350 | -0.003 | 0.01  |
| 6  | 248.650 | 248.665 | 12.3540 | 12.3588 | 0.013  | -0.04 |
| 6  | 253.030 | 253.042 | 14.0430 | 13.9889 | -0.139 | 0.39  |
| 6  | 258.800 | 258.809 | 16.4210 | 16.3679 | -0.122 | 0.32  |
| 6  | 263.280 | 263.286 | 18.4480 | 18.4078 | -0.085 | 0.22  |
| 6  | 268.730 | 268.732 | 21.1350 | 21.1317 | -0.101 | 0.25  |
| 6  | 273.090 | 273.090 | 23.5440 | 23.5147 | -0.051 | 0.12  |
| 6  | 278.040 | 278.638 | 26.8370 | 26.8276 | -0.015 | 0.04  |
| 6  | 283.580 | 283.576 | 30.1360 | 30.0575 | -0.071 | 0.16  |
| 6  | 288.260 | 288.254 | 33.4680 | 33.3800 | -0.119 | 0.26  |

NP = 20, RMSPCT = 0.274

| ID | T,XPTL  | T-68    | P,ATM     | CALCD     | DEL T  | P,PCT |
|----|---------|---------|-----------|-----------|--------|-------|
| 8  | 110.000 | 109.998 | 0.0007500 | 0.0007205 | -0.319 | 5.49  |
| 8  | 120.000 | 119.989 | 0.0034600 | 0.0034295 | -0.063 | 0.89  |
| 8  | 130.000 | 129.987 | 0.012720  | 0.012540  | -0.121 | 1.44  |
| 8  | 140.000 | 139.992 | 0.037850  | 0.037359  | -0.131 | 1.31  |
| 8  | 150.000 | 150.000 | 0.095500  | 0.094657  | -0.116 | 1.00  |
| 8  | 160.000 | 160.010 | 0.21200   | 0.21068   | -0.084 | 0.63  |
| 8  | 170.000 | 170.019 | 0.42360   | 0.42214   | -0.053 | 0.35  |
| 8  | 180.000 | 180.027 | 0.77780   | 0.77628   | -0.034 | 0.20  |
| 8  | 190.000 | 190.032 | 1.3300    | 1.3297    | -0.004 | 0.02  |
| 8  | 200.000 | 200.035 | 2.1462    | 2.1472    | 0.011  | -0.05 |
| 8  | 210.000 | 210.033 | 3.2970    | 3.2998    | 0.020  | -0.08 |
| 8  | 220.000 | 220.030 | 4.8580    | 4.8639    | 0.033  | -0.12 |
| 8  | 230.000 | 230.025 | 6.9120    | 6.9196    | 0.032  | -0.11 |
| 8  | 240.000 | 240.020 | 9.5510    | 9.5508    | -0.001 | 0.00  |
| 8  | 250.000 | 250.014 | 12.8500   | 12.8456   | -0.012 | 0.03  |
| 8  | 260.000 | 260.008 | 16.9100   | 16.8973   | -0.028 | 0.08  |
| 8  | 270.000 | 270.001 | 21.8000   | 21.8066   | 0.012  | -0.03 |
| 8  | 280.000 | 279.997 | 27.6500   | 27.6895   | 0.062  | -0.14 |
| 8  | 290.000 | 289.994 | 34.6500   | 34.6843   | 0.045  | -0.10 |

NP = 19, RMSPCT = 1.383

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Table 5. Calculated Ethane Vapor Pressures.

NAME

R. D. Goodwin

DATE

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## ETHANE VAPOR PRESSURES

| T, K    | P, ATM    | DP/DT     | D2P/DT2    |
|---------|-----------|-----------|------------|
| 89.399  | 0.0000096 | 0.0000026 | 0.0000063  |
| 90.000  | 0.0000099 | 0.0000026 | 0.0000064  |
| 95.000  | 0.0000346 | 0.0000083 | 0.00000177 |
| 100.000 | 0.0001067 | 0.0000226 | 0.00000430 |
| 105.000 | 0.0002916 | 0.0000555 | 0.00000942 |
| 110.000 | 0.0007207 | 0.0001239 | 0.00001881 |
| 115.000 | 0.0016337 | 0.0002545 | 0.00003475 |
| 120.000 | 0.0034347 | 0.0004868 | 0.00005997 |
| 125.000 | 0.0067608 | 0.0008749 | 0.00009759 |
| 130.000 | 0.012559  | 0.001489  | 0.0001508  |
| 135.000 | 0.022167  | 0.002414  | 0.0002228  |
| 140.000 | 0.037390  | 0.003753  | 0.0003164  |
| 145.000 | 0.060574  | 0.005618  | 0.0004339  |
| 150.000 | 0.094653  | 0.008135  | 0.0005771  |
| 155.000 | 0.14323   | 0.01143   | 0.000747   |
| 160.000 | 0.21052   | 0.01565   | 0.000944   |
| 165.000 | 0.30146   | 0.02091   | 0.001167   |
| 170.000 | 0.42162   | 0.02736   | 0.001415   |
| 175.000 | 0.57722   | 0.03511   | 0.001688   |
| 180.000 | 0.77507   | 0.04428   | 0.001984   |
| 185.000 | 1.0226    | 0.0550    | 0.00230    |
| 190.000 | 1.3276    | 0.0673    | 0.00263    |
| 195.000 | 1.6984    | 0.0813    | 0.00298    |
| 200.000 | 2.1439    | 0.0972    | 0.00335    |
| 205.000 | 2.6731    | 0.1148    | 0.00372    |
| 210.000 | 3.2954    | 0.1344    | 0.00411    |
| 215.000 | 4.0205    | 0.1560    | 0.00451    |
| 220.000 | 4.8585    | 0.1795    | 0.00492    |
| 225.000 | 5.8194    | 0.2052    | 0.00533    |
| 230.000 | 6.9136    | 0.2329    | 0.00576    |
| 235.000 | 8.1519    | 0.2628    | 0.00619    |
| 240.000 | 9.5450    | 0.2948    | 0.00664    |
| 245.000 | 11.1040   | 0.3292    | 0.00710    |
| 250.000 | 12.8406   | 0.3658    | 0.00757    |
| 255.000 | 14.7664   | 0.4049    | 0.00806    |
| 260.000 | 16.8936   | 0.4465    | 0.00858    |
| 265.000 | 19.2357   | 0.4907    | 0.00913    |
| 270.000 | 21.8056   | 0.5378    | 0.00972    |
| 275.000 | 24.6190   | 0.5880    | 0.01036    |
| 280.000 | 27.6914   | 0.6416    | 0.01108    |
| 285.000 | 31.0410   | 0.6990    | 0.01192    |
| 290.000 | 34.6890   | 0.7610    | 0.01294    |
| 295.000 | 38.6612   | 0.8289    | 0.01429    |
| 300.000 | 42.9922   | 0.9053    | 0.01649    |
| 305.000 | 47.7442   | 1.0029    | 0.022894   |
| 305.330 | 48.0779   | 1.0160    | 0.000000   |

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Table 6. Reduced Vapor Pressure Functions.

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## ETHANE REDUCED VAPOR PRESSURE FUNCTIONS

| T, K    | X    | Y       | (Y-X)   |
|---------|------|---------|---------|
| 89.399  | 0.00 | 0.00000 | 0.00000 |
| 91.186  | 0.02 | 0.02199 | 0.00199 |
| 92.510  | 0.04 | 0.04392 | 0.00392 |
| 93.873  | 0.06 | 0.06578 | 0.00578 |
| 95.277  | 0.08 | 0.08759 | 0.00759 |
| 96.723  | 0.10 | 0.10934 | 0.00934 |
| 98.215  | 0.12 | 0.13102 | 0.01102 |
| 99.753  | 0.14 | 0.15264 | 0.01264 |
| 101.339 | 0.16 | 0.17419 | 0.01419 |
| 102.977 | 0.18 | 0.19568 | 0.01568 |
| 104.669 | 0.20 | 0.21710 | 0.01710 |
| 106.418 | 0.22 | 0.23845 | 0.01845 |
| 108.226 | 0.24 | 0.25972 | 0.01972 |
| 110.096 | 0.26 | 0.28093 | 0.02093 |
| 112.032 | 0.28 | 0.30205 | 0.02205 |
| 114.037 | 0.30 | 0.32310 | 0.02310 |
| 116.116 | 0.32 | 0.34406 | 0.02406 |
| 118.272 | 0.34 | 0.36495 | 0.02495 |
| 120.509 | 0.36 | 0.38574 | 0.02574 |
| 122.832 | 0.38 | 0.40645 | 0.02645 |
| 125.247 | 0.40 | 0.42706 | 0.02706 |
| 127.759 | 0.42 | 0.44758 | 0.02758 |
| 130.373 | 0.44 | 0.46800 | 0.02800 |
| 133.097 | 0.46 | 0.48832 | 0.02832 |
| 135.937 | 0.48 | 0.50854 | 0.02854 |
| 138.901 | 0.50 | 0.52866 | 0.02866 |
| 141.997 | 0.52 | 0.54866 | 0.02866 |
| 145.234 | 0.54 | 0.56855 | 0.02855 |
| 148.622 | 0.56 | 0.58833 | 0.02833 |
| 152.172 | 0.58 | 0.60800 | 0.02800 |
| 155.896 | 0.60 | 0.62755 | 0.02755 |
| 159.807 | 0.62 | 0.64698 | 0.02698 |
| 163.919 | 0.64 | 0.66629 | 0.02629 |
| 168.248 | 0.66 | 0.68548 | 0.02548 |
| 172.812 | 0.68 | 0.70455 | 0.02455 |
| 177.530 | 0.70 | 0.72350 | 0.02350 |
| 182.725 | 0.72 | 0.74233 | 0.02233 |
| 188.121 | 0.74 | 0.76105 | 0.02105 |
| 193.845 | 0.76 | 0.77965 | 0.01965 |
| 199.928 | 0.78 | 0.79815 | 0.01815 |
| 206.405 | 0.80 | 0.81655 | 0.01655 |
| 213.317 | 0.82 | 0.83486 | 0.01486 |
| 220.707 | 0.84 | 0.85309 | 0.01309 |
| 228.627 | 0.86 | 0.87126 | 0.01126 |
| 237.138 | 0.88 | 0.88938 | 0.00938 |
| 246.306 | 0.90 | 0.90749 | 0.00749 |
| 256.212 | 0.92 | 0.92552 | 0.00562 |
| 266.948 | 0.94 | 0.94381 | 0.00381 |
| 278.623 | 0.96 | 0.96216 | 0.00216 |
| 291.366 | 0.98 | 0.98078 | 0.00078 |
| 305.330 | 1.00 | 1.00000 | 0.00000 |

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## PROGRAM PSATFIT

```

C  ETHANE VAPOR PRESSURES,  X = (1-TT/T)/(1-TT/TC),
C  LN(P/PTRP) = A1*X + A2*X2 + A3*X3 + A4*X4 + A5*X*(1-X)**E.
C  AUTHORS ID = (1)TICKNER, (2)ROSSINI, (3)CARRUTH, (4)PAL/POPE,
C  (5)LOOMIS, (6)PORTER, (7)ZIEGLER, (8)BARKELEW/TESTER
C  (9)POPE, (10)DOUSLIN,PREPRINT(1973).
C
COMMON TTRP,TCRT,PTRP, E,A(9), FZ,F1,F2, DLPDT,D2LPDT2
COMMON/999/NFUN,Y,F(30)
DIMENSION TEMP(130),DELT(130)
DIMENSION IO(999),T(999),TX(999),P(999)
DIMENSION G(30)
1  FORMAT(I5, 2F10.0)
2  FORMAT(1H1 17X *ETHANE VAPOR PRESSURES, E =* F5.2//
1  18X 6HTTRP =F7.3, 8H, TCRT =F8.3//
2  18X 12HPTRP,MUATM =F9.5, 12H, PCRT,ATM =F9.5// 2(15X 3F16.9// )
3  FORMAT( 18X 2HID 4X6HT,XPTL 6X4HT-68 7X5HP,ATM 7X5HCALCD
1  5X5HDEL T 5X5HP,PCT)
4  FORMAT(1H1 17X 24ID 4X6HT,XPTL 6X4HT-68 7X5HP,ATM 7X5HCALCD
1  5X5HDEL T 5X5HP,PCT)
5  FORMAT(15X I5, 2F10.3, 2F12.7, F10.3, F10.2)
6  FORMAT(15X I5, 2F10.3, 2F12.6, F10.3, F10.2)
7  FORMAT(15X I5, 2F10.3, 2F12.5, F10.3, F10.2)
8  FORMAT(15X I5, 2F10.3, 2F12.4, F10.3, F10.2)
9  FORMAT(1H0 17X 4HNP =I4, 10H, RMSPCT =F7.3)
10 FORMAT(F8.0, F9.0, 63X)
11 FORMAT(1H1 16X *ETHANE VAPOR PRESSURES* // 17X3HT,K 6X5HP,ATM
1  6X5HDP/DT 5X7HD2P/DT2 )
12 FORMAT(10X F10.3, 2F11.7, F12.8)
13 FORMAT(10X F10.3, 2F11.6, F12.7)
14 FORMAT(10X F10.3, 2F11.5, F12.6)
15 FORMAT(10X F10.3, 2F11.4, F12.5)
16 FORMAT(1H1 15X *ETHANE REDUCED VAPOR PRESSURE FUNCTIONS* //
1  17X 3HT,K 7X1HX 9X1HY 5X5H(Y-X) )
17 FORMAT(10X F10.3, F8.2, 2F10.5)
18 FORMAT(16X 2H6P 6X2HSS)
19 FORMAT(10X 2F10.4)
C  READ-IN THE T48 - T68 TEMP. CONVERSION TABLE.
20 READ 10, ((TEMP(J),DELT(J)),J=1,130)
21 TTRP=89.899 $ TCRT=305.33 $ PTRP=9.638E-6 $ E=1.5 $ N=0
C
C  READ (7)ZIEGLER, KELVIN, MM HG.
22 DO 24 J=1,99 $ READ 1, IO,TT,PP $ IF(IO) 23,25
23 N = N+1 $ IO(N)=IO $ P(N)=PP/760 $ TX(N)=TT
24 T(N) = T68(TT,DELT,TEMP)
25 NF1 = N
C  READ MIXED (4)PAL, (9)POPE, (10)DOUSLIN DATA.
C  (4)KELVIN,PSIA, (9)KELVIN,ATMOS, (10)CENTIG.,ATMOS.
26 DO 35 J=1,203 $ READ 1, IO,TT,PP $ IF(IO) 27,36
27 N = N+1 $ IO(N) = IO $ IF(IO-4) 28,30
28 IF(IO-9) 34,32
30 P(N) = PP/14.69595 $ T(N) = T68(TT,DELT,TEMP)
31 TX(N) = TT $ GO TO 35
32 P(N) = PP $ T(N) = T68(TT,DELT,TEMP)
33 TX(N) = TT $ GO TO 35

```



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```

34 P(N) = PP $ T(N) = TX(N) = TT + 273.15
35 CONTINUE
36 NP = N $ NF = 5
C READ (1) DATA, CENTIGRADE, MM HG.
38 DO 43 J=1,99 $ READ 1, IDD,TT,PP $ IF(IDD) 39,41
39 N = N+1 $ ID(N) = IDD $ P(N) = PP/760 $ TX(N) = 273.15 + TT
40 T(N) = T68(TX(N),DELT,TEMP)
41 NP2 = N
C READ (2) DATA, CENTIGRADE, MM HG.
42 DO 44 J=1,99 $ READ 1, IDD,TT,PP $ IF(IDD) 43,45
43 N = N+1 $ ID(N) = IDD $ P(N) = PP/760 $ TX(N) = 273.15 + TT
44 T(N) = T68(TX(N),DELT,TEMP)
45 NP3 = N
C READ (3) DATA, KELVIN, MM HG.
46 DO 48 J=1,99 $ READ 1, IDD,TT,PP $ IF(IDD) 47,49
47 N = N+1 $ ID(N) = IDD $ P(N) = PP/760 $ TX(N) = TT
48 T(N) = T68(TT,DELT,TEMP)
49 NP4 = N
C READ (5) DATA, KELVIN, ATMOS.
50 DO 52 J=1,99 $ READ 1, IDD,TT,PP $ IF(IDD) 51,53
51 N = N+1 $ ID(N) = IDD $ P(N) = PP $ TX(N) = TT
52 T(N) = T68(TT,DELT,TEMP)
53 NP5 = N
C READ (6) DATA, KELVIN, ATMOS.
54 DO 56 J=1,99 $ READ 1, IDD,TT,PP $ IF(IDD) 55,57
55 N = N+1 $ ID(N) = IDD $ P(N) = PP $ TX(N) = TT
56 T(N) = T68(TT,DELT,TEMP)
57 NP6 = N
C READ (8) DATA, KELVIN, ATMOS.
60 DO 62 J=1,99 $ READ 1, IDD,TT,PP $ IF(IDD) 61,63
61 N = N+1 $ ID(N)=IDD $ P(N)=PP $ TX(N)=TT
62 T(N) = T68(TT,DELT,TEMP)
63 NPP = NP7 = N
C
C EXPLORE VALUES FOR PTRP.
79 E = 1.6 $ PRINT 18 $ SSK = 1.0E+010
80 XK = 1 - TTRP/TCRT
81 DO 92 IP=1,25 $ PTR = 9.600 + 0.001*IP $ PTRP = PTR*1.0E-6
82 NFUN = NF $ DO 85 J=1,NP $ X = (1-TTRP/T(J))/XK
83 F(1)=X $ F(2)=X**2 $ F(3)=X**3 $ F(4)=X**4 $ F(5)=X*(1-X)**E
84 Y = LOGF(P(J)/PTRP)
85 CALL FIT $ CALL COEFF $ SS = 0 $ DO 86 K=1,9
86 A(K) = F(K)
87 DO 38 J=1,NP $ PC=PSATF(T(J)) $ SS = SS+(P(J)/PC-1)**2
88 CONTINUE $ SS=100*SQR(TF(SS/NP)) $ IF(SS.LT.SSK) 89,92
89 SSK=SS $ EK=E $ TCK=TCRT $ TTK=TTRP $ PTK=PTRP
90 DO 31 K=1,9
91 G(K) = F(K)
92 PRINT 19, PTR, SS
93 E=EK $ TCRT=TCK $ TTRP=TTK $ PTRP=PTK $ DO 94 K=1,9
94 A(K) = G(K) $ FCRT = PTRP*EXP(F(A(1)+A(2)+A(3)+A(4)))
95 PTR = 1.0E6*PTRP

```



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C PRINT DEVIATIONS, INCLUDING  $DT = -DP/(DP/DT)$ .

```

105 L = 9 $ SS = 0
106 PRINT 2, E, TTRP, TCRT, PTR, PCRT, (A(K), K=1,6) $ PRINT 3
107 DO 125 J=1, NP $ L = L+1 $ IF(L-57) 112, 108
108 L = 0 $ PRINT 4
112 PC = PSATF(T(J)) $ DPDT = PC*DLPDT
113 DP = P(J)-PC $ DT = -DP/DPDT
114 PCT = 100*DP/PC $ SS = SS + PCT**2
117 IF(PC-0.01) 120, 118, 118
118 IF(PC-0.1) 121, 119, 119
119 IF(PC-1.0) 122, 123, 123
120 PRINT 5, ID(J), TX(J), T(J), P(J), PC, DT, PCT $ GOTO 125
121 PRINT 6, ID(J), TX(J), T(J), P(J), PC, DT, PCT $ GOTO 125
122 PRINT 7, ID(J), TX(J), T(J), P(J), PC, DT, PCT $ GOTO 125
123 PRINT 8, ID(J), TX(J), T(J), P(J), PC, DT, PCT
125 CONTINUE
126 SS = SQRTF(SS/NP) $ PRINT 9, NP, SS

```

C

C PRINT OTHER DATA DEVIATIONS.

```

140 K = NP+1 $ SS = N = 0 $ PRINT 4
141 DO 157 J=K, NPP $ IF(J-NPP) 143, 142
142 SS = SQRTF(SS/N) $ PRINT 9, N, SS $ GO TO 158
143 N = N+1 $ PC=PSATF(T(J)) $ DPDT = PC*DLPDT
144 DP = P(J)-PC $ DT = -DP/DPDT
145 PCT = 100*DP/PC $ SS = SS + PCT**2
146 IF(PC-0.01) 150, 147, 147
147 IF(PC-0.1) 151, 148, 148
148 IF(PC-1.0) 152, 153, 153
150 PRINT 5, ID(J), TX(J), T(J), P(J), PC, DT, PCT $ GO TO 155
151 PRINT 6, ID(J), TX(J), T(J), P(J), PC, DT, PCT $ GO TO 155
152 PRINT 7, ID(J), TX(J), T(J), P(J), PC, DT, PCT $ GO TO 155
153 PRINT 8, ID(J), TX(J), T(J), P(J), PC, DT, PCT
155 IF(ID(J+1)-ID(J)) 156, 157
156 SS = SQRTF(SS/N) $ PRINT 9, N, SS $ SS=N=0 $ PRINT 4
157 CONTINUE
158 CONTINUE

```

C

C PRINTOUT UNIFORM TABLE FOR PUBLICATION.

```

200 PRINT 11 $ DO 220 J=1, 46 $ IF(J-1) 202, 201
201 TT = TTRP $ GO TO 205
202 IF(J-46) 204, 203
203 TT = TCRT $ GO TO 205
204 TT = 80 + 5*J
205 PS=PSATF(TT) $ DPDT=PS*DLPDT $ D2PDT2=PS*(DLPDT**2 + D2LDPDT2)
207 IF(PS-0.01) 210, 208, 208
208 IF(PS-0.1) 211, 209, 209
209 IF(PS-1.0) 212, 213, 213
210 PRINT 12, TT, PS, DPDT, D2PDT2 $ GOTO 220
211 PRINT 13, TT, PS, DPDT, D2PDT2 $ GOTO 220
212 PRINT 14, TT, PS, DPDT, D2PDT2 $ GOTO 220
213 IF(J-46) 215, 214
214 D2PDT2 = 0
215 PRINT 15, TT, PS, DPDT, D2PDT2
220 CONTINUE

```

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C   PRINT UNIFORM REDUCED TABLE.
C   Y = LN(P/PTRP)/YN,   YN = LN(PCRT/PTRP).
C   YC = (A(1)*X + . . . + A(5)*X*(1-X)**E)/YN.
250 XN = 1-TTRP/TCRT $ YN = A(1) + A(2) + A(3) + A(4)
251 PRINT 16 $ DO 270 J=1,51 $ X = 0.02*(J-1)
252 IF(J-1) 254,253
253 TT = TTRP $ GOTO 257
254 IF(J-51) 256,255
255 TT = TCRT $ GOTO 257
256 TT = TTRP/(1-X*XN)
257 IF(J-51) 259,258
258 Z = 0 $ GO TO 260
259 Z = X*(1-X)**E
260 YC = A(5)*Z $ DO 261 K=1,4
261 YC = YC + A(K)*X**K
262 YC = YC/YN $ YX = YC - X
270 PRINT 17, TT, X, YC, YX
999 CONTINUE $ STOP $ END

```

SINGLE-BANK COMPILATION.

```

      FUNCTION PSATF(T)
C   LN(P/PTRP) = A1*X + A2*X2 + A3*X3 + A4*X4 + A5*X*(1-X)**E.
C   ARGUMENT, X = (1-TT/T)/(1-TT/TC).
C   YIELDS ALSO DLPDT = (DP/DT)/P, AND D2LPT = (D2P/DT2)/P.
      COMMON TTRP,TCRT,PTRP, E,A(9), FZ,F1,F2, DLPDT,D2LPDT2
1   FORMAT(1H3 9X *PSATF = 0, T EXCEEDS TCRT. * / )
2   XN=1-TTRP/TCRT $ X=(1-TTRP/T)/XN $ X2=X**2 $ X3=X**3 $ X4=X**4
3   DXDT = TTRP/XN/T**2 $ D2XDT2 = -2*DXDT/T
4   Q = 1-X $ IF(Q) 5,5,7
5   PSATF = DLPDT = D2LPDT2 = 0 $ PRINT 1 $ RETURN
6   Z = Z1 = Z2 = 0 $ GOTO 9
7   W = Q**E $ W1 = -E*W/Q $ W2 = (1-E)*W1/Q
8   Z = X*W $ Z1 = X*W1 + W $ Z2 = X*W2 + 2*W1
9   FZ = A(1)*X + A(2)*X2 + A(3)*X3 + A(4)*X4 + A(5)*Z
10  PSATF = PTRP*EXP(FZ)
11  F1 = A(1) + 2*A(2)*X + 3*A(3)*X2 + 4*A(4)*X3 + A(5)*Z1
12  DLPDT = F1*DXDT
13  F2 = 2*A(2) + 6*A(3)*X + 12*A(4)*X2 + A(5)*Z2
15  D2LPDT2 = F1*D2XDT2 + F2*DXDT**2 $ RETURN $ END

```

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FUNCTION T68(X,YMAT,XMAT)

THIS PROGRAM HAS BEEN CHANGED SO THAT THE OSCILLATING NATURE OF THE MATRIX TO BE INTERPOLATED EXISTS ONLY AT THE UPPER END OF THE TABLE

THIS ROUTINE WILL TAKE INPUT MATRICES OF UP TO 999 ELEMENTS EACH, ARRANGED SO THAT THE X MATRIX(XMAT) IS IN EITHER ASCENDING OR DESCENDING ORDER, SELECT NMAX OF THESE POINTS, CHOSEN SO THAT SUCCESSIVE X VALUES OSCILLATE ABOUT THE VALUE OF THE ARGUMENT X UNLESS THE ENDS OF THE XMATRIX INTERFERE (IN THIS CASE THE OSCILLATORY NATURE IS LOST BUT THE PROGRAM WILL STILL PERFORM AN INTERPOLATION), INTERPOLATE ON THESE NMAX PAIRS OF DATA BY AN OSCILLATING VARIABLE POINT AITKEN INTERPOLATION ALGORITHM EITHER UNTIL THE PERCENTAGE CHANGE IN THE INTERPOLANT IS LESS THAN THE ACRCY ARGUMENT (THE ARGUMENT NESSY INDICATES THE NUMBER OF THE POINT JUST BEFORE THE LAST ONE CHECKED) OR UNTIL THE NMAX POINTS ARE ALL USED. IT IS SUGGESTED THAT NMAX BE LESS THAN 10, AND OF COURSE LESS THAN NELMTS. NELMTS INDICATES THE NUMBER OF ELEMENTS IN XMAT OR YMAT.

IF NESSY IS ZERO IT INDICATES THAT THE INTERPOLATION REQUIREMENT HAS NOT BEEN SATISFIED. IF NESSY IS 1 IT MEANS THAT THE VALUE OF X LIES OUTSIDE THE RANGE OF XMAT.

DIMENSION YMAT(999), XMAT(999), A(21,20)

100 FORMAT(42HINTERPOLATION REQUIREMENT NOT SATISFIED(X=,E16.8,1H)/33H

1LAST 2 APPROXIMATIONS OF Y ARE(Y=,E16.8,1H,,E16.8,1H))

200 FORMAT(55HTHIS REPRESENTS AN EXTRAPOLATION OF THE XMAT MATRIX(X=,E16.8,1H)/33HNO CALCULATION HAS BEEN PERFORMED)

300 FORMAT(24HNELMTS IS LESS THAN NMAX)

400 FORMAT(22HNMAX IS LARGER THAN 20)

NELMTS=130 \$ NMAX=9 \$ ACRCY=0.01

IF(NMAX-20)71,71,69

69 WRITE OUTPUT TAPE 6,4)0

T68 = X \$ RETURN

71 IF(NMAX-NELMTS)75,75,73

73 WRITE OUTPUT TAPE 6,3)0

T68 = X \$ RETURN

75 CONTINUE

FIRST TWO SUCCESSIVE VALUES OF THE XMATRIX THAT STRADDLE THE VALUE X WILL BE SOUGHT

JJ1=NELMTS-1

DO 2) I=1,JJ1

DIF1=X-XMAT(I)

DIF2=XMAT(I+1)-X

IF(DIF1)16,15,16

15 T68 = X + YMAT(I)

NESSY =NMAX

RETURN

16 IF(DIF2)18,17,18

17 T68 = X + YMAT(I+1)

NESSY =NMAX

RETURN

18 RATIO=DIF1/ DIF2

IF(RATIO)20,20,19

19 IM10=I

GO TO 32

20 CONTINUE

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      AT THIS POINT ONE COULD PRINT THE FOLLOWING STATEMENT
      WRITE OUTPUT TAPE 6,200,X
      NESSY=1
      T68 = X $ RETURN
32  CONTINUE
      NOTE THAT RATIO IS POSITIVE IF THE TWO POINTS STRADDLE X
      REGARDLESS WHICH IS LARGER
      JJJ=IMID
      JUP=IMID
      JDN=IMID
      IF(JJJ+NMAX-NELMTS+1)38,98,102
98  DO 201 J=1,NMAX
      JJJ=IMID+J-1
      A(1,J)=XMAT(JJJ)
201  A(2,J)=YMAT(JJJ)
      GO TO 203
102  DO 41 J=1,NMAX
      JJ=J/2
      JOE=J-2*JJ
      JOE IS 0 IF J IS EVEN AND 1 IF J IS ODD
      IF(J-1)33,40,33
33  IF(JDN-1)34,36,34
34  IF(JUP-NELMTS)35,37,35
35  IF(JOE)37,36,37
36  JUP=JUP+1
      JJJ=JUP
      GO TO 40
37  JDN=JDN-1
      JJJ=JDN
      GO TO 40
40  A(1,J)=XMAT(JJJ)
      A(2,J)=YMAT(JJJ)
41  CONTINUE
203  NNN=NMAX+1
      DO 6 J=3,NNN
      L=J-1
      DO 5 K=L,NMAX
      J IS THE COLUMN NUMBER
      K IS THE ROW NUMBER
      A(J,K)=(A(J-1,K)-A(J-1,J-2))*(X-A(1,J-2))/(A(1,K)-A(1,J-2))
1      +A(J-1,J-2)
      IF(K-L)3,2,3
2  IF(ABSF((A(J,L)-A(J-1,L-1))/A(J,L))-ACRCY/100.0)7,7,3
3  CONTINUE
5  CONTINUE
6  CONTINUE
      NESSY=0
      AT THIS POINT ONE COULD PRINT OUT THE FOLLOWING STATEMENT.
      WRITE OUTPUT TAPE 6,100,X,A(NNN,NMAX),A(NNN-1,NMAX-1)
      T68 = X + A(NNN,NMAX)
      RETURN
7  NESSY=J-1
      T68 = X + A(J,L) $ RETURN $ END

```

*This program by  
Rolf Prydz.*



|                                                         |         |             |           |              |               |          |      |
|---------------------------------------------------------|---------|-------------|-----------|--------------|---------------|----------|------|
| Cryogenics Division - NBS Institute for Basic Standards |         |             |           |              | PROJECT NO.   | FILE NO. | PAGE |
| LABORATORY NOTE                                         |         |             |           |              | 2750364       | 73-3     | 20   |
| SUBJECT                                                 |         |             |           |              | NAME          |          |      |
| The Vapor Pressures of Ethane                           |         |             |           |              | R. D. Goodwin |          |      |
|                                                         |         |             |           |              | DATE          |          |      |
|                                                         |         |             |           |              | July 9, 1973  |          |      |
| ETHANE VAPOR PRESSURES, E = 1.50                        |         |             |           |              |               |          |      |
| TTRP = 89.899, TCRT = 305.330                           |         |             |           |              |               |          |      |
| PTRP, MUATM = 9.96700, PCRT, ATM = 48.07723             |         |             |           |              |               |          |      |
| 10.806922651                                            |         | 8.344715938 |           | -3.119603823 |               |          |      |
| -0.642995191                                            |         | 6.059966098 |           | 0.000000000  |               |          |      |
| ID                                                      | T, XPTL | T-68        | P, ATM    | CALCD        | DEL T         | P, PCT   |      |
| 7                                                       | 90.000  | 90.010      | 0.0000103 | 0.0000103    | 0.000         | -0.01    |      |
| 7                                                       | 100.000 | 100.010     | 0.0001098 | 0.0001098    | -0.001        | 0.01     |      |
| 7                                                       | 110.000 | 109.998     | 0.0007364 | 0.0007363    | -0.001        | 0.02     |      |
| 7                                                       | 120.000 | 119.989     | 0.0034934 | 0.0034939    | 0.001         | -0.01    |      |
| 7                                                       | 130.000 | 129.987     | 0.012728  | 0.012732     | 0.003         | -0.04    |      |
| 7                                                       | 140.000 | 139.992     | 0.037792  | 0.037803     | 0.003         | -0.03    |      |
| 7                                                       | 150.000 | 150.000     | 0.095474  | 0.095476     | 0.000         | -0.00    |      |
| 7                                                       | 160.000 | 160.010     | 0.21196   | 0.21192      | -0.003        | 0.02     |      |
| 7                                                       | 170.000 | 170.019     | 0.42387   | 0.42369      | -0.007        | 0.04     |      |
| 7                                                       | 180.000 | 180.027     | 0.77824   | 0.77783      | -0.009        | 0.05     |      |
| 7                                                       | 184.520 | 184.550     | 1.00000   | 0.99944      | -0.010        | 0.06     |      |
| 9                                                       | 198.181 | 198.216     | 1.9737    | 1.9761       | 0.027         | -0.12    |      |
| 4                                                       | 214.302 | 214.334     | 3.9209    | 3.9159       | -0.032        | 0.13     |      |
| 4                                                       | 224.102 | 224.130     | 5.6367    | 5.6402       | 0.017         | -0.06    |      |
| 4                                                       | 229.756 | 229.782     | 6.8569    | 6.8598       | 0.012         | -0.04    |      |
| 4                                                       | 234.558 | 234.581     | 8.0335    | 8.0392       | 0.022         | -0.07    |      |
| 9                                                       | 234.692 | 234.715     | 8.0741    | 8.0741       | -0.000        | 0.00     |      |
| 10                                                      | 238.150 | 238.150     | 9.0097    | 9.0077       | -0.007        | 0.02     |      |
| 9                                                       | 238.771 | 238.792     | 9.1843    | 9.1905       | 0.021         | -0.07    |      |
| 4                                                       | 239.844 | 239.864     | 9.4959    | 9.5019       | 0.020         | -0.06    |      |
| 4                                                       | 240.514 | 240.534     | 9.6960    | 9.7003       | 0.014         | -0.04    |      |
| 10                                                      | 243.150 | 243.150     | 10.5063   | 10.5045      | -0.006        | 0.02     |      |
| 4                                                       | 243.359 | 243.377     | 10.5760   | 10.5764      | 0.001         | -0.00    |      |
| 4                                                       | 246.814 | 246.830     | 11.7137   | 11.7162      | 0.007         | -0.02    |      |
| 4                                                       | 247.816 | 247.831     | 12.0502   | 12.0628      | 0.036         | -0.10    |      |
| 10                                                      | 248.150 | 248.150     | 12.1756   | 12.1747      | -0.003        | 0.01     |      |
| 4                                                       | 249.741 | 249.755     | 12.7620   | 12.7496      | -0.034        | 0.10     |      |
| 4                                                       | 250.146 | 250.160     | 12.8985   | 12.8976      | -0.002        | 0.01     |      |
| 4                                                       | 251.587 | 251.600     | 13.4425   | 13.4344      | -0.022        | 0.06     |      |
| 4                                                       | 252.544 | 252.556     | 13.8065   | 13.7997      | -0.018        | 0.05     |      |
| 10                                                      | 253.150 | 253.150     | 14.0310   | 14.0301      | -0.002        | 0.01     |      |
| 4                                                       | 254.290 | 254.301     | 14.4898   | 14.4848      | -0.012        | 0.03     |      |
| 4                                                       | 257.543 | 257.552     | 15.8252   | 15.8266      | 0.003         | -0.01    |      |
| 10                                                      | 258.150 | 258.150     | 16.0835   | 16.0827      | -0.002        | 0.00     |      |
| 10                                                      | 263.150 | 263.150     | 18.3464   | 18.3452      | -0.003        | 0.01     |      |
| 4                                                       | 263.380 | 263.386     | 18.4543   | 18.4573      | 0.006         | -0.02    |      |
| 4                                                       | 267.536 | 267.539     | 20.5197   | 20.5145      | -0.010        | 0.03     |      |
| 10                                                      | 268.150 | 268.150     | 20.8318   | 20.8308      | -0.002        | 0.00     |      |
| 4                                                       | 271.749 | 271.750     | 22.7661   | 22.7662      | 0.000         | -0.00    |      |
| 9                                                       | 272.949 | 272.949     | 23.4515   | 23.4394      | -0.021        | 0.05     |      |
| 10                                                      | 273.150 | 273.150     | 23.5549   | 23.5536      | -0.002        | 0.01     |      |
| 4                                                       | 275.922 | 275.921     | 25.1584   | 25.1702      | 0.020         | -0.05    |      |
| 4                                                       | 276.363 | 276.362     | 25.4558   | 25.4347      | -0.035        | 0.08     |      |
| 4                                                       | 276.385 | 276.384     | 25.4491   | 25.4479      | -0.002        | 0.00     |      |
| 4                                                       | 276.514 | 276.513     | 25.5472   | 25.5257      | -0.036        | 0.08     |      |
| 4                                                       | 277.813 | 277.811     | 26.3185   | 26.3189      | 0.001         | -0.00    |      |
| 10                                                      | 278.150 | 278.150     | 26.5309   | 26.5290      | -0.003        | 0.01     |      |



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SUBJECT

The Vapor Pressure of Ethane

NAME

R. D. Goodwin

DATE

July 9, 1973

| ID | T,XPTL  | T-68    | P,ATM   | CALCD   | DEL T  | P,PCT |
|----|---------|---------|---------|---------|--------|-------|
| 4  | 280.041 | 280.038 | 27.7039 | 27.7217 | 0.028  | -0.06 |
| 4  | 282.247 | 282.243 | 29.1537 | 29.1647 | 0.016  | -0.04 |
| 10 | 283.150 | 283.150 | 29.7763 | 29.7739 | -0.003 | 0.01  |
| 4  | 284.635 | 284.630 | 30.7664 | 30.7893 | 0.033  | -0.07 |
| 9  | 284.845 | 284.840 | 30.9555 | 30.9353 | -0.029 | 0.07  |
| 4  | 287.653 | 287.648 | 32.9289 | 32.9392 | 0.014  | -0.03 |
| 10 | 288.150 | 288.150 | 33.3110 | 33.3080 | -0.004 | 0.01  |
| 4  | 288.263 | 288.257 | 33.3899 | 33.3872 | -0.004 | 0.01  |
| 4  | 290.040 | 290.034 | 34.6873 | 34.7192 | 0.042  | -0.09 |
| 9  | 290.214 | 290.208 | 34.8748 | 34.8518 | -0.030 | 0.07  |
| 4  | 292.236 | 292.229 | 36.4440 | 36.4216 | -0.028 | 0.06  |
| 4  | 293.098 | 293.091 | 37.0816 | 37.1074 | 0.032  | -0.07 |
| 10 | 293.150 | 293.150 | 37.1583 | 37.1547 | -0.005 | 0.01  |
| 9  | 293.266 | 293.259 | 37.2672 | 37.2422 | -0.031 | 0.07  |
| 4  | 296.347 | 296.339 | 39.7598 | 39.7852 | 0.030  | -0.06 |
| 10 | 298.150 | 298.150 | 41.3494 | 41.3446 | -0.005 | 0.01  |
| 4  | 299.665 | 299.657 | 42.6543 | 42.6808 | 0.030  | -0.06 |
| 9  | 299.863 | 299.855 | 42.8863 | 42.8591 | -0.030 | 0.06  |
| 4  | 300.205 | 300.196 | 43.1650 | 43.1686 | 0.004  | -0.01 |
| 4  | 301.251 | 301.242 | 44.1085 | 44.1274 | 0.020  | -0.04 |
| 10 | 302.150 | 302.150 | 44.9809 | 44.9751 | -0.006 | 0.01  |
| 10 | 303.150 | 303.150 | 45.9327 | 45.9268 | -0.006 | 0.01  |
| 4  | 303.471 | 303.462 | 46.2032 | 46.2273 | 0.025  | -0.05 |
| 4  | 303.477 | 303.468 | 46.2798 | 46.2331 | -0.048 | 0.10  |
| 9  | 304.012 | 304.002 | 46.7736 | 46.7533 | -0.021 | 0.04  |
| 4  | 304.049 | 304.039 | 46.7698 | 46.7896 | 0.020  | -0.04 |
| 10 | 304.150 | 304.150 | 46.9040 | 46.8987 | -0.005 | 0.01  |
| 4  | 304.360 | 304.350 | 47.0931 | 47.0953 | 0.002  | -0.00 |
| 4  | 304.446 | 304.435 | 47.2198 | 47.1802 | -0.040 | 0.08  |
| 4  | 304.519 | 304.508 | 47.2025 | 47.2525 | 0.050  | -0.11 |
| 4  | 304.734 | 304.723 | 47.4310 | 47.4661 | 0.035  | -0.07 |
| 4  | 304.796 | 304.785 | 47.5185 | 47.5280 | 0.009  | -0.02 |
| 4  | 304.924 | 304.913 | 47.6846 | 47.6560 | -0.028 | 0.06  |
| 4  | 304.980 | 304.969 | 47.7131 | 47.7122 | -0.001 | 0.00  |
| 4  | 305.121 | 305.110 | 47.8496 | 47.8541 | 0.004  | -0.01 |
| 10 | 305.150 | 305.150 | 47.8992 | 47.8945 | -0.005 | 0.01  |
| 4  | 305.153 | 305.142 | 47.8807 | 47.8864 | 0.006  | -0.01 |
| 10 | 305.250 | 305.250 | 47.9994 | 47.9958 | -0.004 | 0.01  |

NP = 85, RMSPCT = 0.050

|                                                       |                               |           |             |               |      |
|-------------------------------------------------------|-------------------------------|-----------|-------------|---------------|------|
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| LABORATORY NOTE                                       |                               |           | 2750364     | 73-3          | 22   |
| SUBJECT                                               | The Vapor Pressures of Ethane |           | NAME        | R. D. Goodwin |      |
|                                                       |                               |           | DATE        | July 9, 1973  |      |
| ETHANE VAPOR PRESSURES                                |                               |           |             |               |      |
| T, K                                                  | P, ATM                        | DP/DT     | D2P/DT2     |               |      |
| 89.899                                                | 0.0000100                     | 0.0000027 | 0.00000064  |               |      |
| 90.000                                                | 0.0000102                     | 0.0000027 | 0.00000066  |               |      |
| 95.000                                                | 0.0000358                     | 0.0000085 | 0.00000181  |               |      |
| 100.000                                               | 0.0001095                     | 0.0000232 | 0.00000439  |               |      |
| 105.000                                               | 0.0002985                     | 0.0000567 | 0.00000960  |               |      |
| 110.000                                               | 0.0007363                     | 0.0001264 | 0.00001915  |               |      |
| 115.000                                               | 0.0016670                     | 0.0002592 | 0.00003529  |               |      |
| 120.000                                               | 0.0034991                     | 0.0004948 | 0.00006077  |               |      |
| 125.000                                               | 0.0068762                     | 0.0008875 | 0.00009864  |               |      |
| 130.000                                               | 0.012752                      | 0.001507  | 0.0001521   |               |      |
| 135.000                                               | 0.022468                      | 0.002439  | 0.0002242   |               |      |
| 140.000                                               | 0.037834                      | 0.003785  | 0.0003177   |               |      |
| 145.000                                               | 0.061192                      | 0.005656  | 0.0004350   |               |      |
| 150.000                                               | 0.095478                      | 0.008177  | 0.0005776   |               |      |
| 155.000                                               | 0.14426                       | 0.01148   | 0.000747    |               |      |
| 160.000                                               | 0.21176                       | 0.01569   | 0.000942    |               |      |
| 165.000                                               | 0.30288                       | 0.02095   | 0.001165    |               |      |
| 170.000                                               | 0.42317                       | 0.02738   | 0.001412    |               |      |
| 175.000                                               | 0.57882                       | 0.03511   | 0.001684    |               |      |
| 180.000                                               | 0.77662                       | 0.04426   | 0.001979    |               |      |
| 185.000                                               | 1.0239                        | 0.0549    | 0.00229     |               |      |
| 190.000                                               | 1.3287                        | 0.0672    | 0.00263     |               |      |
| 195.000                                               | 1.6991                        | 0.0812    | 0.00298     |               |      |
| 200.000                                               | 2.1440                        | 0.0970    | 0.00334     |               |      |
| 205.000                                               | 2.6726                        | 0.1147    | 0.00372     |               |      |
| 210.000                                               | 3.2943                        | 0.1343    | 0.00411     |               |      |
| 215.000                                               | 4.0188                        | 0.1558    | 0.00451     |               |      |
| 220.000                                               | 4.8561                        | 0.1794    | 0.00492     |               |      |
| 225.000                                               | 5.8165                        | 0.2051    | 0.00534     |               |      |
| 230.000                                               | 6.9105                        | 0.2329    | 0.00577     |               |      |
| 235.000                                               | 8.1487                        | 0.2628    | 0.00620     |               |      |
| 240.000                                               | 9.5420                        | 0.2949    | 0.00665     |               |      |
| 245.000                                               | 11.1016                       | 0.3293    | 0.00711     |               |      |
| 250.000                                               | 12.8390                       | 0.3660    | 0.00758     |               |      |
| 255.000                                               | 14.7659                       | 0.4052    | 0.00807     |               |      |
| 260.000                                               | 16.8947                       | 0.4468    | 0.00858     |               |      |
| 265.000                                               | 19.2381                       | 0.4910    | 0.00913     |               |      |
| 270.000                                               | 21.8098                       | 0.5381    | 0.00971     |               |      |
| 275.000                                               | 24.6242                       | 0.5882    | 0.01034     |               |      |
| 280.000                                               | 27.6972                       | 0.6416    | 0.01105     |               |      |
| 285.000                                               | 31.0467                       | 0.6989    | 0.01187     |               |      |
| 290.000                                               | 34.6934                       | 0.7607    | 0.01288     |               |      |
| 295.000                                               | 38.6630                       | 0.8283    | 0.01425     |               |      |
| 300.000                                               | 42.9905                       | 0.9046    | 0.01657     |               |      |
| 305.000                                               | 47.7433                       | 1.0055    | 0.03283     |               |      |
| 305.330                                               | 48.0772                       | 1.0228    | 0.00000     |               |      |

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SUBJECT

The Vapor Pressures of Ethane

NAME

R. D. Goodwin

DATE

July 9, 1973

## ETHANE REDUCED VAPOR PRESSURE FUNCTIONS

| T, K    | X    | Y       | (Y-X)   |
|---------|------|---------|---------|
| 89.899  | 0.00 | 0.00000 | 0.00000 |
| 91.186  | 0.02 | 0.02190 | 0.00190 |
| 92.510  | 0.04 | 0.04376 | 0.00376 |
| 93.873  | 0.06 | 0.06558 | 0.00558 |
| 95.277  | 0.08 | 0.08734 | 0.00734 |
| 96.723  | 0.10 | 0.10906 | 0.00906 |
| 98.215  | 0.12 | 0.13073 | 0.01073 |
| 99.753  | 0.14 | 0.15234 | 0.01234 |
| 101.339 | 0.16 | 0.17389 | 0.01389 |
| 102.977 | 0.18 | 0.19538 | 0.01538 |
| 104.669 | 0.20 | 0.21680 | 0.01680 |
| 106.418 | 0.22 | 0.23816 | 0.01816 |
| 108.226 | 0.24 | 0.25945 | 0.01945 |
| 110.096 | 0.26 | 0.28066 | 0.02066 |
| 112.032 | 0.28 | 0.30180 | 0.02180 |
| 114.037 | 0.30 | 0.32285 | 0.02285 |
| 116.116 | 0.32 | 0.34382 | 0.02382 |
| 118.272 | 0.34 | 0.36471 | 0.02471 |
| 120.509 | 0.36 | 0.38551 | 0.02551 |
| 122.832 | 0.38 | 0.40621 | 0.02621 |
| 125.247 | 0.40 | 0.42682 | 0.02682 |
| 127.759 | 0.42 | 0.44733 | 0.02733 |
| 130.373 | 0.44 | 0.46774 | 0.02774 |
| 133.097 | 0.46 | 0.48805 | 0.02805 |
| 135.937 | 0.48 | 0.50825 | 0.02825 |
| 138.901 | 0.50 | 0.52835 | 0.02835 |
| 141.997 | 0.52 | 0.54833 | 0.02833 |
| 145.234 | 0.54 | 0.56820 | 0.02820 |
| 148.622 | 0.56 | 0.58796 | 0.02796 |
| 152.172 | 0.58 | 0.60760 | 0.02760 |
| 155.896 | 0.60 | 0.62713 | 0.02713 |
| 159.807 | 0.62 | 0.64654 | 0.02654 |
| 163.919 | 0.64 | 0.66583 | 0.02583 |
| 168.248 | 0.66 | 0.68501 | 0.02501 |
| 172.812 | 0.68 | 0.70406 | 0.02406 |
| 177.630 | 0.70 | 0.72301 | 0.02301 |
| 182.725 | 0.72 | 0.74184 | 0.02184 |
| 188.121 | 0.74 | 0.76056 | 0.02056 |
| 193.845 | 0.76 | 0.77917 | 0.01917 |
| 199.928 | 0.78 | 0.79769 | 0.01769 |
| 206.405 | 0.80 | 0.81611 | 0.01611 |
| 213.317 | 0.82 | 0.83445 | 0.01445 |
| 220.707 | 0.84 | 0.85272 | 0.01272 |
| 228.627 | 0.86 | 0.87093 | 0.01093 |
| 237.138 | 0.88 | 0.88910 | 0.00910 |
| 246.306 | 0.90 | 0.90726 | 0.00726 |
| 256.212 | 0.92 | 0.92544 | 0.00544 |
| 266.948 | 0.94 | 0.94369 | 0.00369 |
| 278.623 | 0.96 | 0.96208 | 0.00208 |
| 291.366 | 0.98 | 0.98074 | 0.00074 |
| 305.330 | 1.00 | 1.00000 | 0.00000 |

## APPENDIX K

|                                                                                   |  |                                            |                  |           |
|-----------------------------------------------------------------------------------|--|--------------------------------------------|------------------|-----------|
| Cryogenics Division - NBS Institute for Basic Standards<br><b>LABORATORY NOTE</b> |  | PROJECT NO.<br>2750364                     | FILE NO.<br>73-4 | PAGE<br>1 |
| SUBJECT<br>Ethane Virial Coefficients and Saturated Vapor Densities               |  | NAME R. D. Goodwin<br>DATE August 14, 1973 |                  |           |

1. Introduction

The virial equation of state for low densities is needed for thermal computations to generate P-ρ-T data, and to obtain saturated vapor densities via the vapor pressure equation.

In this report we develop analytical representations for the virial coefficients of ethane and obtain the corresponding saturated vapor densities.

In the truncated virial equation,

$$Z(T, d) \equiv P/(R \cdot T \cdot d) = 1 + B(x) \cdot \sigma + C(x) \cdot \sigma^2 + D(x) \cdot \sigma^3, \quad (1)$$

P is pressure, R the gas constant, T the absolute temperature, d the density, and  $\sigma \equiv d/d_c$  is reduced density. The second, third, and fourth coefficients B(x), C(x), D(x) are dimensionless functions of reduced temperature  $x \equiv T/T_c$ . We use  $T_c \approx 305.33$  K, and  $V_c \approx 1/d_c = 145.56$  cc/mol from Douslin [2]. In the tables we use symbols B\*, C\* and D\* for the coefficients of (1).

2. The Second Virial Coefficient

Data for B(x) through about 1960 are reviewed by Tester [16]. Since then we have data from Gunn [8], Hoover [9], Pope [15], McGlashan [12], and Douslin [2]. Data of Gunn and of Douslin extend from 273 K upwards to 623 K. McGlashan gives outstanding experimental work on the hydrocarbon series (but not on ethane) down to  $T/T_c = 0.5$ . From his formulations he concludes that the low-temperature data of Eucken and Parts [4] are wrong. This suspicion also was expressed by Ziegler et al. [17].

For least squares we have selected for low temperatures only the data from McGlashan's formula because all other data diverge widely therefrom (Table 2). For high temperatures we have selected Douslin's recent data because the experimental work [2] was executed with great care. Table 2 shows that Michels (1D=3) and Gunn (1D=8) are in substantial agreement with Douslin. For consistency with Douslin, we have increased the absolute values of McGlashan's data by one percent, well within the uncertainty of his  $V_c = 148$  cc/mol.



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## SUBJECT

Ethane Virial Coefficients and Saturated Vapor Densities

NAME

R. D. Goodwin

DATE

August 14, 1973

Our formula for  $B(x)$ , selected from many variations, finally is similar to that developed for methane [6],

$$B(x) = \left[ B_1 + B_2/x^{1/4} + B_3/x + B_4/x^2 + B_5/x^3 \right] \cdot \left[ 1 - (T_0/T)^{1/4} \right], \quad (2)$$

$$T_0 = 740.0 \text{ K},$$

$$B_3 = 9.21 \ 7322,$$

$$B_1 = 7.99 \ 3156,$$

$$B_4 = -2.48 \ 1668,$$

$$B_2 = -10.67 \ 2497,$$

$$B_5 = 0.84 \ 2328.$$

Table 1 gives results for (2) with the data used for least squares: (6) McGlashan; (10) Douslin. Data not used for  $\ell_s$  are compared with (2) in Table 2: (1) Eucken; (2) Lambert; (3) Michels; (4) Hoover; (5) Pope; (8) Gunn.

### 3. The Third Virial Coefficient

For  $C(x)$  relatively few data are known to us. The data of Michels [13] and Hoover [9] were generalized in 1967 by Chueh [1], using a formula similar to that developed by Goodwin [5]. In 1971 Pope [15] gave five low-temperature values from 210 to 306 K. For temperatures above 273 K we are fortunate to have the recent, carefully-derived data of Douslin [2].

A comparison of Chueh's generalized function with Douslin's data at  $T/T_c = 2$  shows  $C^* = 0.20$  (Chueh), and  $C^* = 0.15$  (Douslin). Whereas the Chueh formula gives nearly constant values at high temperatures, the Douslin data are trending asymptotically toward zero.

For least squares we have selected the data of Douslin at high temperatures, and data generated by Chueh's formula at low temperatures. For consistency we have diminished these latter values by two percent. (Chueh fails to give his critical densities.) At low temperatures the third virial coefficient is not important in the computation of eq (1) because the maximum possible density (saturated vapor) is diminishing exponentially with temperature,  $e^{-\gamma/T}$ , (see Table 4).

|                                                                                   |  |                         |                  |           |
|-----------------------------------------------------------------------------------|--|-------------------------|------------------|-----------|
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Our formula for  $C(x)$  is much simpler than that of Chueh, and is similar to that developed for methane [6],

$$C(x) = \left[ C_1/x + C_2/x^3 + C_3/x^5 \right] \cdot (1 - T_o/T), \quad (3)$$

$$T_o = 217.80 \text{ K}, \quad C_2 = 0.865 \text{ 299},$$

$$C_1 = 0.253 \text{ 773}, \quad C_3 = 0.556 \text{ 075}.$$

Least squares results are in the upper part of Table 3: (7) Chueh; (10) Douslin. Other data in the lower part are: (4) Hoover; (5) Pope.

#### 4. The Fourth Virial Coefficient

Recent data of Douslin [2] are plotted in Figure 1. The general behavior expected for  $D^*$  is shown in the book by Mason and Spurling [11]. As present data exist only at  $T > T_c$ , we use the simple formula,

$$100 \cdot D^* = x^{-1/4} \cdot \exp[a - b/(x-1)], \quad (4)$$

where  $x \equiv T/T_c$ , and  $a = 4.00$ ,  $b = 1.84$  from Figure 1.

#### 5. Examination of the Virial Equation

It is valuable to know the relative importance of the terms of eq (1). In Table 4 we compute these for the saturated vapor, using densities from the formula of Plank and Kambeitz quoted by Tester [16]. We have increased the P.K. densities by 0.088% to agree with the virial equation at 90 K. Pressures are from our vapor pressure equation [7].

In the fourth column of Table 4 we give the ratio  $DI/DN$  of ideal gas density to the P.K. calculated densities. Fifth and sixth columns give  $B(x) \cdot \sigma$  and  $C(x) \cdot \sigma^2$ . If all data were accurate, we should expect  $Z(T, d)$  in the last column to be the same as  $DI/DN$ .

The vapor pressures of Ziegler [17] were based on second virial coefficients of Eucken and Parts [4], the accuracy of which Ziegler questioned. Our selection for  $B^*$  also disagrees with Eucken and Parts. We therefore have recomputed our vapor

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pressure constants using alternate vapor pressure data of Ziegler, as shown in the addendum to our Laboratory Note [7]. This revised vapor pressure equation is used in the following to obtain the densities of saturated vapor.

## 6. Derivation of the Saturated Vapor Densities

For a given temperature we iterate density in the virial equation to obtain a pressure therefrom which is the same as the vapor pressure. Results are in Table 5. In previous work we have found that this method gives acceptable results at densities up to about  $\rho_c/3$ , which for ethane occurs near  $T = 286$  K. We see that data from the Plank-Kambeitz formula diverge increasingly from our results on approach to  $T_c$ . The highest temperature at which our results are accurate remains to be seen by comparison with data from other sources. Figure 2 shows, however, that in the region of overlap with Douslin's vapor densities [2], our results (the filled circles) appear reasonable.

Figure 3 shows the results at lower temperatures. We see that powers of  $(1/T)$  greater than the first will be needed to describe these data.

## 7. Discussion of Uncertainties

Experimental uncertainties for virial coefficients vary inversely as the significance of these coefficients in giving departure from ideal gas behavior, see Table 4. For the second coefficient only, for example,

$$\delta B/B = \frac{\delta Z}{Z} \cdot \frac{Z}{Z-1},$$

where  $\delta B$  and  $\delta Z$  are small variations in  $B$  and  $Z$ . Assume a tolerable error of 0.01 percent in  $Z$ . From Table 4 we compute the approximate tolerable uncertainty in  $B$ , neglecting the effect of  $C(T)$ ,

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| <u>T, K</u> | <u>mol/l</u> | <u><math>\delta B/B</math>, %</u> |
|-------------|--------------|-----------------------------------|
| 100         | 0.000013     | 357.0                             |
| 120         | 0.000349     | 21.6                              |
| 140         | 0.00327      | 3.37                              |
| 160         | 0.01626      | 0.915                             |
| 180         | 0.05434      | 0.352                             |
| 200         | 0.1401       | 0.170                             |
| 220         | 0.3035       | 0.096                             |
| 240         | 0.5864       | 0.060                             |
| 260         | 1.057        | 0.040                             |

Not all authors give estimates of uncertainty for experimental virial coefficients. Hoover et al, however, give these estimates for ethane,

| <u>T, K</u> | <u><math>\delta B/B</math>, %</u> | <u><math>\delta C/C</math>, %</u> |
|-------------|-----------------------------------|-----------------------------------|
| 215         | 1.0                               | 10.0                              |
| 240         | 0.4                               | 4.0                               |
| 273         | 0.1                               | 1.0                               |

and we believe these to be reasonable estimates for very careful work. In Table 2, however, we see that Hoover's data, ID=4, differ from our selection by up to five per cent at low temperatures (215 and 240 K).

Our derived densities depend on the vapor pressure equation. This we estimate to be uncertain by several percent at the lowest temperatures approaching the triple point. The virial equation, on the other hand, approaches ideal gas behavior at these low temperatures. At the higher temperatures above 270 K, we believe the virial coefficients and vapor pressures of Douslin to be accurate as can be derived from the best of PVT measurements.



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## Table Captions

Table 1. Second virial data of (6) McGlashan, (10) Douslin.

Table 2. Second virial, (1) Eucken, (2) Lambert, (3) Michels, (4) Hoover, (5) Pope, (8) Gunn.

Table 3. Third virial, (7) Chueh, (10) Douslin, (4) Hoover, (5) Pope.

Table 4. Terms of the virial equation for saturated vapor.

Table 5. Saturated vapor densities derived via V.P. and virial equations.

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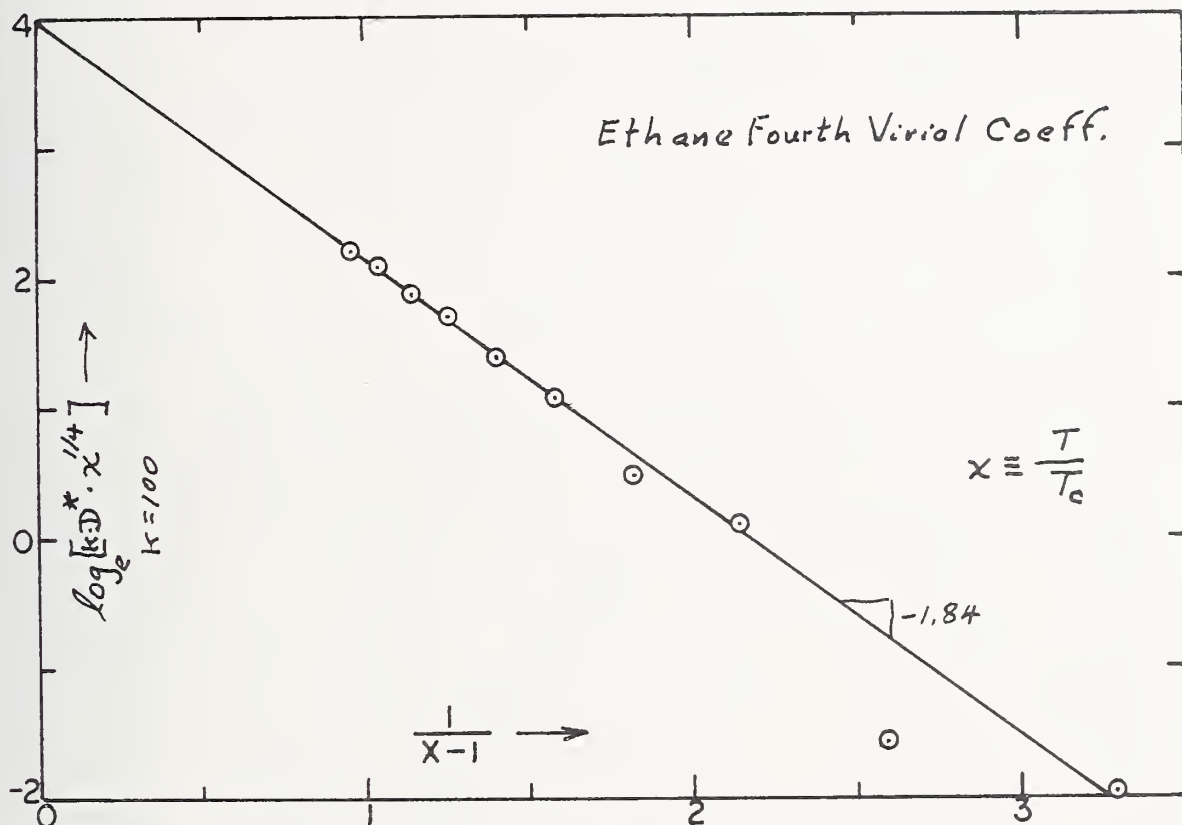


Figure 1. Ethane fourth virial coefficients of Douslin [2],

$$100 \cdot D^* = x^{-1/4} \cdot \exp[4.0 - 1.84/(x-1)].$$

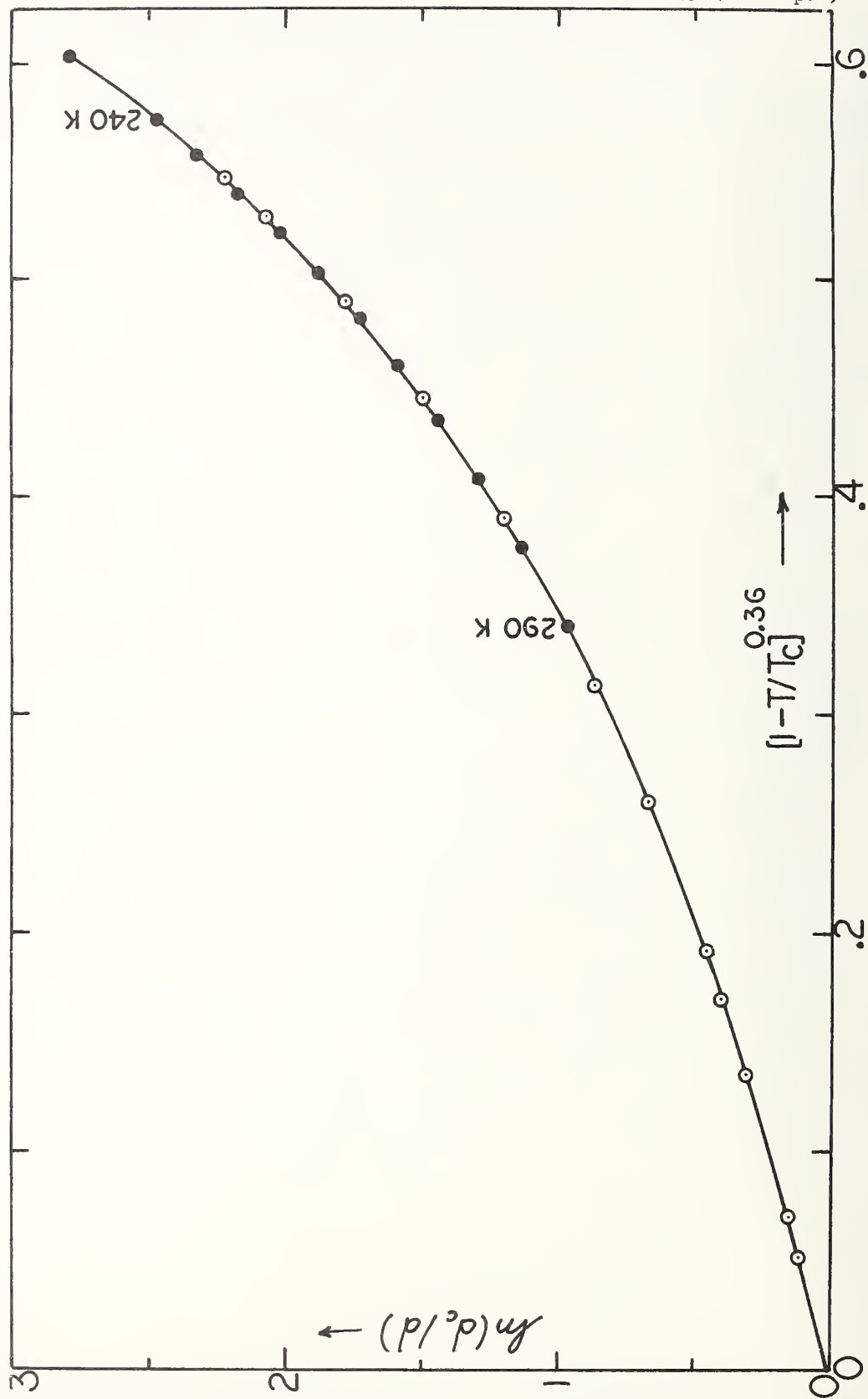


Figure 2. Ethane saturated vapor densities. Open circles from Douslin [2]; filled circles from Table 5, this report.

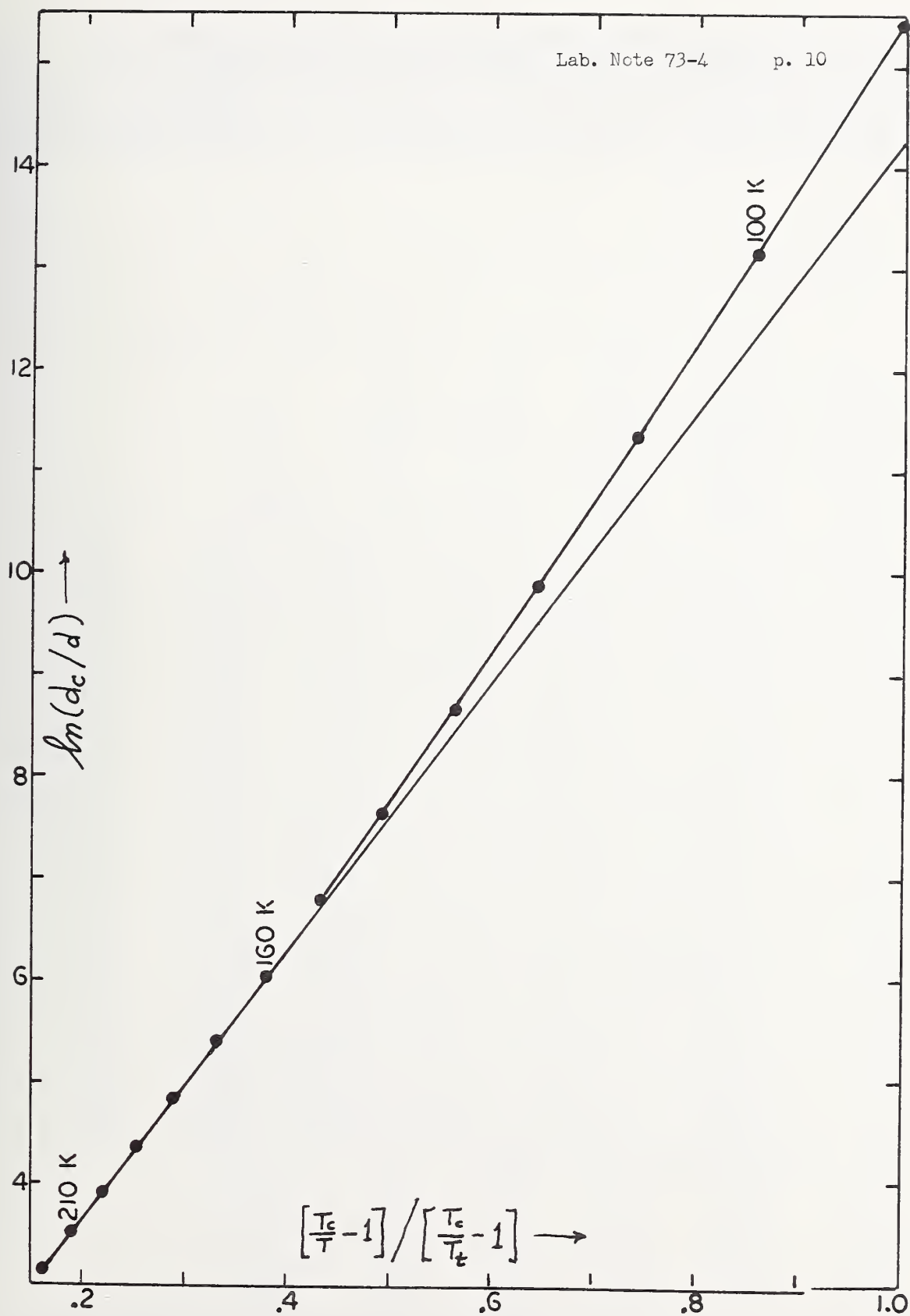


Figure 3. Ethane saturated vapor densities from Table 5, this report.

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Table 1. Second virial data of (6) McGlashan, (10) Douslin.

## ETHANE SECOND VIRIAL COEFFICIENT

EB = 0.250, TZ = 740.0

7.993156 -10.672497 9.217322 -2.481668 0.842328

| ID | T, K    | T/TC   | B*     | CALC   | DIFF   | PCNT  |
|----|---------|--------|--------|--------|--------|-------|
| 6  | 150.000 | 0.4913 | -5.309 | -5.310 | 0.001  | 0.01  |
| 6  | 160.000 | 0.5240 | -4.598 | -4.597 | -0.001 | -0.01 |
| 6  | 170.000 | 0.5568 | -4.031 | -4.030 | -0.001 | -0.02 |
| 6  | 180.000 | 0.5895 | -3.569 | -3.569 | -0.000 | -0.01 |
| 6  | 190.000 | 0.6223 | -3.188 | -3.188 | 0.000  | 0.01  |
| 6  | 200.000 | 0.6550 | -2.868 | -2.869 | 0.001  | 0.02  |
| 6  | 210.000 | 0.6878 | -2.597 | -2.597 | 0.001  | 0.03  |
| 6  | 220.000 | 0.7205 | -2.353 | -2.364 | 0.001  | 0.03  |
| 6  | 230.000 | 0.7533 | -2.161 | -2.162 | 0.000  | 0.02  |
| 6  | 240.000 | 0.7860 | -1.984 | -1.984 | -0.000 | -0.00 |
| 6  | 250.000 | 0.8188 | -1.828 | -1.828 | -0.001 | -0.04 |
| 6  | 260.000 | 0.8515 | -1.690 | -1.688 | -0.002 | -0.09 |
| 10 | 273.150 | 0.8946 | -1.527 | -1.527 | 0.001  | 0.06  |
| 10 | 298.150 | 0.9765 | -1.276 | -1.275 | -0.001 | -0.08 |
| 10 | 303.150 | 0.9929 | -1.232 | -1.232 | -0.001 | -0.05 |
| 10 | 323.150 | 1.0584 | -1.077 | -1.076 | -0.001 | -0.06 |
| 10 | 348.150 | 1.1402 | -0.914 | -0.914 | 0.001  | 0.08  |
| 10 | 373.150 | 1.2221 | -0.780 | -0.781 | 0.001  | 0.10  |
| 10 | 398.150 | 1.3040 | -0.668 | -0.670 | 0.001  | 0.16  |
| 10 | 423.150 | 1.3859 | -0.574 | -0.575 | 0.000  | 0.06  |
| 10 | 448.150 | 1.4678 | -0.493 | -0.493 | 0.000  | 0.10  |
| 10 | 473.150 | 1.5496 | -0.423 | -0.422 | -0.000 | -0.08 |
| 10 | 498.150 | 1.6315 | -0.360 | -0.360 | -0.000 | -0.01 |
| 10 | 523.150 | 1.7134 | -0.306 | -0.305 | -0.001 | -0.27 |
| 10 | 548.150 | 1.7953 | -0.256 | -0.256 | -0.000 | -0.19 |
| 10 | 573.150 | 1.8771 | -0.212 | -0.212 | -0.001 | -0.30 |
| 10 | 598.150 | 1.9590 | -0.172 | -0.172 | -0.000 | -0.02 |
| 10 | 623.150 | 2.0409 | -0.135 | -0.135 | 0.001  | 0.53  |

NP = 28, MEANPCT = 0.088



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Table 2. Second Virial, (1) Eucken, (2) Lambert, (3) Michels, (4) Hoover  
(5) Pope, (8) Gunn.

| ID | T, K    | T/TC   | B*     | CALC   | DIFF   | PCNT  |
|----|---------|--------|--------|--------|--------|-------|
| 1  | 200.000 | 0.6550 | -3.112 | -2.869 | -0.243 | -8.48 |
| 2  | 200.000 | 0.6550 | -3.119 | -2.869 | -0.250 | -8.72 |
| 5  | 209.534 | 0.6863 | -2.533 | -2.609 | 0.076  | 2.93  |
| 1  | 210.000 | 0.6878 | -2.817 | -2.597 | -0.219 | -8.44 |
| 2  | 210.000 | 0.6878 | -2.817 | -2.597 | -0.219 | -8.44 |
| 4  | 215.000 | 0.7042 | -2.340 | -2.477 | 0.137  | 5.52  |
| 1  | 220.000 | 0.7205 | -2.542 | -2.364 | -0.178 | -7.52 |
| 2  | 220.000 | 0.7205 | -2.576 | -2.364 | -0.212 | -8.97 |
| 1  | 230.000 | 0.7533 | -2.288 | -2.162 | -0.126 | -5.84 |
| 2  | 230.000 | 0.7533 | -2.343 | -2.162 | -0.181 | -8.38 |
| 5  | 238.769 | 0.7820 | -1.972 | -2.005 | 0.033  | 1.63  |
| 1  | 240.000 | 0.7860 | -2.095 | -1.984 | -0.111 | -5.61 |
| 2  | 240.000 | 0.7860 | -2.116 | -1.984 | -0.132 | -6.65 |
| 4  | 240.000 | 0.7860 | -1.900 | -1.984 | 0.085  | 4.26  |
| 1  | 250.000 | 0.8188 | -1.924 | -1.828 | -0.096 | -5.26 |
| 2  | 250.000 | 0.8188 | -1.944 | -1.828 | -0.117 | -6.39 |
| 5  | 254.807 | 0.8345 | -1.733 | -1.759 | 0.026  | 1.45  |
| 1  | 250.000 | 0.8515 | -1.759 | -1.688 | -0.070 | -4.17 |
| 2  | 250.000 | 0.8515 | -1.786 | -1.688 | -0.098 | -5.80 |
| 1  | 270.000 | 0.8843 | -1.614 | -1.564 | -0.051 | -3.23 |
| 2  | 270.000 | 0.8843 | -1.649 | -1.564 | -0.085 | -5.43 |
| 3  | 273.150 | 0.8946 | -1.521 | -1.527 | 0.006  | 0.39  |
| 4  | 273.150 | 0.8946 | -1.535 | -1.527 | -0.007 | -0.48 |
| 5  | 273.150 | 0.8946 | -1.507 | -1.527 | 0.020  | 1.33  |
| 8  | 273.200 | 0.8948 | -1.527 | -1.527 | 0.000  | 0.02  |
| 1  | 280.000 | 0.9170 | -1.470 | -1.452 | -0.018 | -1.25 |
| 2  | 280.000 | 0.9170 | -1.511 | -1.452 | -0.059 | -4.09 |
| 2  | 290.000 | 0.9498 | -1.408 | -1.351 | -0.058 | -4.26 |
| 3  | 298.138 | 0.9764 | -1.275 | -1.275 | 0.000  | 0.03  |
| 8  | 298.200 | 0.9766 | -1.284 | -1.275 | -0.009 | -0.71 |
| 2  | 300.000 | 0.9825 | -1.305 | -1.259 | -0.046 | -3.68 |
| 5  | 306.062 | 1.0024 | -1.204 | -1.207 | 0.003  | 0.27  |
| 3  | 322.748 | 1.0570 | -1.078 | -1.079 | 0.001  | 0.07  |
| 8  | 323.200 | 1.0585 | -1.032 | -1.076 | -0.006 | -0.60 |
| 3  | 347.652 | 1.1386 | -0.916 | -0.917 | 0.002  | 0.19  |
| 3  | 372.522 | 1.2201 | -0.784 | -0.784 | 0.001  | 0.09  |
| 8  | 377.600 | 1.2367 | -0.752 | -0.760 | 0.008  | 1.10  |
| 3  | 397.844 | 1.3030 | -0.671 | -0.671 | -0.001 | -0.08 |
| 8  | 410.900 | 1.3458 | -0.616 | -0.619 | 0.004  | 0.61  |
| 3  | 422.700 | 1.3844 | -0.576 | -0.576 | -0.000 | -0.04 |
| 8  | 444.300 | 1.4551 | -0.508 | -0.505 | -0.003 | -0.69 |
| 8  | 477.600 | 1.5642 | -0.423 | -0.411 | -0.013 | -3.09 |
| 8  | 510.900 | 1.6733 | -0.350 | -0.331 | -0.019 | -5.83 |

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| ID | T, K    | T/TC   | B*     | CALC   | DIFF   | PCNT  |
|----|---------|--------|--------|--------|--------|-------|
| 6  | 150.000 | 0.4913 | -5.309 | -5.310 | 0.001  | 0.01  |
| 6  | 160.000 | 0.5240 | -4.598 | -4.597 | -0.001 | -0.01 |
| 6  | 170.000 | 0.5568 | -4.031 | -4.030 | -0.001 | -0.02 |
| 6  | 180.000 | 0.5895 | -3.569 | -3.569 | -0.000 | -0.01 |
| 6  | 190.000 | 0.6223 | -3.188 | -3.188 | 0.000  | 0.01  |
| 6  | 200.000 | 0.6550 | -2.868 | -2.869 | 0.001  | 0.02  |
| 6  | 210.000 | 0.6878 | -2.597 | -2.597 | 0.001  | 0.03  |
| 6  | 220.000 | 0.7205 | -2.353 | -2.364 | 0.001  | 0.03  |
| 6  | 230.000 | 0.7533 | -2.161 | -2.162 | 0.000  | 0.02  |
| 6  | 240.000 | 0.7860 | -1.984 | -1.984 | -0.000 | -0.00 |
| 6  | 250.000 | 0.8188 | -1.828 | -1.828 | -0.001 | -0.04 |
| 6  | 250.000 | 0.8515 | -1.690 | -1.688 | -0.002 | -0.09 |
| 10 | 273.150 | 0.8946 | -1.527 | -1.527 | 0.001  | 0.06  |
| 10 | 298.150 | 0.9765 | -1.276 | -1.275 | -0.001 | -0.08 |
| 10 | 303.150 | 0.9929 | -1.232 | -1.232 | -0.001 | -0.05 |
| 10 | 323.150 | 1.0584 | -1.077 | -1.076 | -0.001 | -0.06 |
| 10 | 348.150 | 1.1402 | -0.914 | -0.914 | 0.001  | 0.08  |
| 10 | 373.150 | 1.2221 | -0.780 | -0.781 | 0.001  | 0.10  |
| 10 | 398.150 | 1.3040 | -0.668 | -0.670 | 0.001  | 0.16  |
| 10 | 423.150 | 1.3859 | -0.574 | -0.575 | 0.000  | 0.06  |
| 10 | 448.150 | 1.4678 | -0.493 | -0.493 | 0.000  | 0.10  |
| 10 | 473.150 | 1.5496 | -0.423 | -0.422 | -0.000 | -0.08 |
| 10 | 498.150 | 1.6315 | -0.360 | -0.360 | -0.000 | -0.01 |
| 10 | 523.150 | 1.7134 | -0.306 | -0.305 | -0.001 | -0.27 |
| 10 | 548.150 | 1.7953 | -0.256 | -0.256 | -0.000 | -0.19 |
| 10 | 573.150 | 1.8771 | -0.212 | -0.212 | -0.001 | -0.30 |
| 10 | 598.150 | 1.9590 | -0.172 | -0.172 | -0.000 | -0.02 |
| 10 | 623.150 | 2.0409 | -0.135 | -0.135 | 0.001  | 0.53  |

NP = 28, MEANPCT = 0.088

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(5) Pope, (8) Gunn.

| ID | T, K    | T/TC   | B*     | CALC   | DIFF   | PCNT  |
|----|---------|--------|--------|--------|--------|-------|
| 1  | 200.000 | 0.6550 | -3.112 | -2.869 | -0.243 | -8.48 |
| 2  | 200.000 | 0.6550 | -3.119 | -2.869 | -0.250 | -8.72 |
| 5  | 209.534 | 0.6863 | -2.533 | -2.609 | 0.076  | 2.93  |
| 1  | 210.000 | 0.6878 | -2.817 | -2.597 | -0.219 | -8.44 |
| 2  | 210.000 | 0.6878 | -2.817 | -2.597 | -0.219 | -8.44 |
| 4  | 215.000 | 0.7042 | -2.340 | -2.477 | 0.137  | 5.52  |
| 1  | 220.000 | 0.7205 | -2.542 | -2.364 | -0.178 | -7.52 |
| 2  | 220.000 | 0.7205 | -2.576 | -2.364 | -0.212 | -8.97 |
| 1  | 230.000 | 0.7533 | -2.288 | -2.162 | -0.126 | -5.84 |
| 2  | 230.000 | 0.7533 | -2.343 | -2.162 | -0.181 | -8.38 |
| 5  | 238.769 | 0.7820 | -1.972 | -2.005 | 0.033  | 1.63  |
| 1  | 240.000 | 0.7860 | -2.095 | -1.984 | -0.111 | -5.61 |
| 2  | 240.000 | 0.7860 | -2.116 | -1.984 | -0.132 | -6.65 |
| 4  | 240.000 | 0.7860 | -1.900 | -1.984 | 0.085  | 4.26  |
| 1  | 250.000 | 0.8188 | -1.924 | -1.828 | -0.096 | -5.26 |
| 2  | 250.000 | 0.8188 | -1.944 | -1.828 | -0.117 | -6.39 |
| 5  | 254.807 | 0.8345 | -1.733 | -1.759 | 0.026  | 1.45  |
| 1  | 250.000 | 0.8515 | -1.759 | -1.688 | -0.070 | -4.17 |
| 2  | 250.000 | 0.8515 | -1.786 | -1.688 | -0.098 | -5.80 |
| 1  | 270.000 | 0.8843 | -1.614 | -1.564 | -0.051 | -3.23 |
| 2  | 270.000 | 0.8843 | -1.649 | -1.564 | -0.085 | -5.43 |
| 3  | 273.150 | 0.8946 | -1.521 | -1.527 | 0.006  | 0.39  |
| 4  | 273.150 | 0.8946 | -1.535 | -1.527 | -0.007 | -0.48 |
| 5  | 273.150 | 0.8946 | -1.507 | -1.527 | 0.020  | 1.33  |
| 8  | 273.200 | 0.8948 | -1.527 | -1.527 | 0.000  | 0.02  |
| 1  | 280.000 | 0.9170 | -1.470 | -1.452 | -0.018 | -1.25 |
| 2  | 280.000 | 0.9170 | -1.511 | -1.452 | -0.059 | -4.09 |
| 2  | 290.000 | 0.9498 | -1.408 | -1.351 | -0.058 | -4.26 |
| 3  | 298.138 | 0.9764 | -1.275 | -1.275 | 0.000  | 0.03  |
| 8  | 298.200 | 0.9766 | -1.284 | -1.275 | -0.009 | -0.71 |
| 2  | 300.000 | 0.9825 | -1.305 | -1.259 | -0.046 | -3.68 |
| 5  | 306.062 | 1.0024 | -1.204 | -1.207 | 0.003  | 0.27  |
| 3  | 322.748 | 1.0570 | -1.078 | -1.079 | 0.001  | 0.07  |
| 8  | 323.200 | 1.0585 | -1.082 | -1.076 | -0.006 | -0.60 |
| 3  | 347.652 | 1.1386 | -0.916 | -0.917 | 0.002  | 0.19  |
| 3  | 372.522 | 1.2201 | -0.784 | -0.784 | 0.001  | 0.09  |
| 8  | 377.600 | 1.2367 | -0.752 | -0.760 | 0.008  | 1.10  |
| 3  | 397.844 | 1.3030 | -0.671 | -0.671 | -0.001 | -0.08 |
| 8  | 410.900 | 1.3458 | -0.616 | -0.619 | 0.004  | 0.61  |
| 3  | 422.700 | 1.3844 | -0.576 | -0.576 | -0.000 | -0.04 |
| 8  | 444.300 | 1.4551 | -0.508 | -0.505 | -0.003 | -0.69 |
| 8  | 477.600 | 1.5642 | -0.423 | -0.411 | -0.013 | -3.09 |
| 8  | 510.900 | 1.6733 | -0.350 | -0.331 | -0.019 | -5.83 |

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## SUBJECT

Ethane Virial Coefficients and Saturated Vapor Densities

## NAME

R. D. Goodwin

## DATE

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Table 3. Third virial, (7) Chueh, (10) Douslin, (4) Hoover, (5) Pope.

## THIRD VIRIAL,

217.800 0.253773 0.865299 0.556075 0.000000

| ID                         | T, K    | T/TCRT | C*     | CALCD  | DIFF   |
|----------------------------|---------|--------|--------|--------|--------|
| 7                          | 210.000 | 0.5878 | -0.251 | -0.247 | -0.004 |
| 7                          | 220.000 | 0.7205 | 0.055  | 0.055  | 0.000  |
| 7                          | 230.000 | 0.7533 | 0.249  | 0.247  | 0.002  |
| 7                          | 240.000 | 0.7860 | 0.367  | 0.366  | 0.001  |
| 7                          | 250.000 | 0.8188 | 0.436  | 0.438  | -0.002 |
| 7                          | 260.000 | 0.8515 | 0.472  | 0.477  | -0.006 |
| 10                         | 273.150 | 0.8946 | 0.489  | 0.499  | -0.010 |
| 10                         | 298.150 | 0.9765 | 0.500  | 0.489  | 0.011  |
| 10                         | 303.150 | 0.9929 | 0.491  | 0.483  | 0.008  |
| 10                         | 323.150 | 1.0584 | 0.455  | 0.453  | 0.003  |
| 10                         | 348.150 | 1.1402 | 0.409  | 0.410  | -0.001 |
| 10                         | 373.150 | 1.2221 | 0.364  | 0.369  | -0.004 |
| 10                         | 398.150 | 1.3040 | 0.328  | 0.332  | -0.003 |
| 10                         | 423.150 | 1.3859 | 0.295  | 0.299  | -0.004 |
| 10                         | 448.150 | 1.4678 | 0.268  | 0.271  | -0.003 |
| 10                         | 473.150 | 1.5496 | 0.250  | 0.247  | 0.002  |
| 10                         | 498.150 | 1.6315 | 0.228  | 0.227  | 0.002  |
| 10                         | 523.150 | 1.7134 | 0.212  | 0.209  | 0.004  |
| 10                         | 548.150 | 1.7953 | 0.195  | 0.193  | 0.002  |
| 10                         | 573.150 | 1.8771 | 0.182  | 0.180  | 0.002  |
| 10                         | 598.150 | 1.9590 | 0.167  | 0.168  | -0.001 |
| 10                         | 623.150 | 2.0409 | 0.154  | 0.157  | -0.003 |
| NP = 22, MEANDIFF = 0.0004 |         |        |        |        |        |

| ID | T, K    | T/TCRT | C*     | CALCD  | DIFF   |
|----|---------|--------|--------|--------|--------|
| 5  | 209.534 | 0.5863 | -2.770 | -0.264 | -2.506 |
| 4  | 215.000 | 0.7042 | -3.356 | -0.079 | -3.277 |
| 5  | 238.769 | 0.7820 | 0.175  | 0.354  | -0.180 |
| 4  | 240.000 | 0.7860 | -0.121 | 0.366  | -0.487 |
| 5  | 254.807 | 0.8345 | 0.401  | 0.460  | -0.059 |
| 5  | 273.150 | 0.8946 | 0.489  | 0.499  | -0.010 |
| 4  | 273.150 | 0.8946 | 0.501  | 0.499  | 0.002  |
| 4  | 273.150 | 0.8946 | 0.537  | 0.499  | 0.038  |
| 4  | 298.138 | 0.9764 | 0.507  | 0.489  | 0.017  |
| 5  | 306.062 | 1.0024 | 0.473  | 0.479  | -0.006 |
| 4  | 322.748 | 1.0570 | 0.456  | 0.453  | 0.003  |
| 4  | 347.652 | 1.1386 | 0.405  | 0.411  | -0.006 |
| 4  | 372.522 | 1.2201 | 0.364  | 0.370  | -0.006 |
| 4  | 397.844 | 1.3030 | 0.330  | 0.332  | -0.002 |
| 4  | 422.700 | 1.3844 | 0.301  | 0.300  | 0.001  |



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Table 4. Terms of the virial equation for saturated vapor.

## TERMS OF THE VIRIAL EQUATION FOR SATURATED VAPOR

| T, K | P, ATM     | MOL/L     | DI/DN    | B*S       | C*S2      | Z(T,D)   |
|------|------------|-----------|----------|-----------|-----------|----------|
| 90   | 0.0000099  | 0.0000013 | 0.999996 | -0.000004 | -0.000000 | 0.999996 |
| 95   | 0.0000348  | 0.0000045 | 0.999987 | -0.000011 | -0.000000 | 0.999989 |
| 100  | 0.0031057  | 0.0000130 | 0.999966 | -0.000028 | -0.000000 | 0.999972 |
| 105  | 0.0002916  | 0.0000338 | 0.999920 | -0.000064 | -0.000000 | 0.999936 |
| 110  | 0.0007207  | 0.0000799 | 0.999831 | -0.000133 | -0.000000 | 0.999867 |
| 115  | 0.0016337  | 0.0001732 | 0.999670 | -0.000256 | -0.000000 | 0.999744 |
| 120  | 0.0034347  | 0.0003490 | 0.999398 | -0.000462 | -0.000000 | 0.999538 |
| 125  | 0.0067608  | 0.0006598 | 0.998969 | -0.000787 | -0.000000 | 0.999213 |
| 130  | 0.0125532  | 0.0011793 | 0.998323 | -0.001276 | -0.000001 | 0.998723 |
| 135  | 0.0221670  | 0.0020063 | 0.997397 | -0.001982 | -0.000002 | 0.998016 |
| 140  | 0.0373903  | 0.0032674 | 0.996119 | -0.002961 | -0.000005 | 0.997034 |
| 145  | 0.0605738  | 0.0051196 | 0.994420 | -0.004276 | -0.000009 | 0.995715 |
| 150  | 0.0946592  | 0.0077508 | 0.992228 | -0.005991 | -0.000016 | 0.993994 |
| 155  | 0.1432275  | 0.0113809 | 0.989479 | -0.008171 | -0.000026 | 0.991803 |
| 160  | 0.2105236  | 0.0162608 | 0.986113 | -0.010882 | -0.000042 | 0.989077 |
| 165  | 0.3014633  | 0.0226721 | 0.982082 | -0.014185 | -0.000063 | 0.985752 |
| 170  | 0.4216243  | 0.0309256 | 0.977343 | -0.018141 | -0.000090 | 0.981769 |
| 175  | 0.5772221  | 0.0413607 | 0.971866 | -0.022806 | -0.000124 | 0.977070 |
| 180  | 0.7750743  | 0.0543439 | 0.965625 | -0.028233 | -0.000164 | 0.971603 |
| 185  | 1.0225573  | 0.0702692 | 0.958606 | -0.034470 | -0.000206 | 0.965324 |
| 190  | 1.3275563  | 0.0895573 | 0.950796 | -0.041563 | -0.000248 | 0.958189 |
| 195  | 1.6984137  | 0.1126577 | 0.942186 | -0.049554 | -0.000281 | 0.950164 |
| 200  | 2.1438795  | 0.1400503 | 0.932771 | -0.058485 | -0.000299 | 0.941217 |
| 205  | 2.6730575  | 0.1722494 | 0.922541 | -0.068395 | -0.000287 | 0.931318 |
| 210  | 3.2953721  | 0.2098093 | 0.911484 | -0.079325 | -0.000230 | 0.920445 |
| 215  | 4.0205218  | 0.2533319 | 0.899587 | -0.091321 | -0.000107 | 0.908571 |
| 220  | 4.8584553  | 0.3034770 | 0.886826 | -0.104432 | 0.000108  | 0.895676 |
| 225  | 5.8193516  | 0.3609763 | 0.873177 | -0.118715 | 0.000448  | 0.881732 |
| 230  | 6.9136108  | 0.4266509 | 0.858605 | -0.134238 | 0.000952  | 0.866714 |
| 235  | 8.1518573  | 0.5014347 | 0.843069 | -0.151085 | 0.001671  | 0.850586 |
| 240  | 9.5449551  | 0.5864036 | 0.826523 | -0.169358 | 0.002667  | 0.833309 |
| 245  | 11.1040386 | 0.6828144 | 0.808912 | -0.189185 | 0.004017  | 0.814832 |
| 250  | 12.8405603 | 0.7921552 | 0.790174 | -0.210725 | 0.005818  | 0.795093 |
| 255  | 14.7663588 | 0.9162120 | 0.770240 | -0.234180 | 0.008194  | 0.774014 |
| 260  | 16.8937542 | 1.0571595 | 0.749033 | -0.259804 | 0.011305  | 0.751500 |
| 265  | 19.2356771 | 1.2176851 | 0.726466 | -0.287925 | 0.015361  | 0.727436 |
| 270  | 21.8058475 | 1.4011641 | 0.702440 | -0.318963 | 0.020642  | 0.701679 |
| 275  | 24.6190249 | 1.6119133 | 0.676839 | -0.353469 | 0.027531  | 0.674063 |
| 280  | 27.6913739 | 1.8555713 | 0.649528 | -0.392177 | 0.036563  | 0.644386 |
| 285  | 31.0410283 | 2.1396901 | 0.620339 | -0.436086 | 0.048505  | 0.612418 |
| 290  | 34.6890345 | 2.4747097 | 0.589059 | -0.486600 | 0.064498  | 0.577898 |
| 295  | 38.6611522 | 2.8756823 | 0.555393 | -0.545771 | 0.086320  | 0.540549 |
| 300  | 42.9921502 | 3.3657409 | 0.518891 | -0.616818 | 0.116916  | 0.500098 |
| 305  | 47.7441963 | 3.9859334 | 0.478608 | -0.705645 | 0.161805  | 0.456160 |



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Table 5. Saturated vapor densities derived via V.P. and virial equations.

## ETHANE SATD. VAPOR DENSITIES VIA V.P. AND VIRIAL EQNS.

| ID | T, K    | P, ATM     | PLANK/KAMB | MOL/L      | PCT   |
|----|---------|------------|------------|------------|-------|
| 1  | 89.899  | 9.9670-006 | 1.3511-006 | 1.3511-006 | 0.00  |
| 1  | 90.000  | 1.0238-005 | 1.3863-006 | 1.3863-006 | 0.00  |
| 1  | 95.000  | 3.5808-005 | 4.5936-006 | 4.5936-006 | 0.00  |
| 1  | 100.000 | 1.0952-004 | 1.3347-005 | 1.3347-005 | 0.00  |
| 1  | 105.000 | 2.9851-004 | 3.4649-005 | 3.4648-005 | 0.00  |
| 1  | 110.000 | 7.3654-004 | 8.1615-005 | 8.1612-005 | 0.00  |
| 1  | 115.000 | 1.6670-003 | 1.7671-004 | 1.7670-004 | 0.01  |
| 1  | 120.000 | 3.4991-003 | 3.5558-004 | 3.5552-004 | 0.01  |
| 1  | 125.000 | 6.8762-003 | 6.7110-004 | 6.7093-004 | 0.02  |
| 1  | 130.000 | 1.2752-002 | 1.1974-003 | 1.1970-003 | 0.04  |
| 1  | 135.000 | 2.2468-002 | 2.0336-003 | 2.0323-003 | 0.06  |
| 1  | 140.000 | 3.7834-002 | 3.3064-003 | 3.3033-003 | 0.09  |
| 1  | 145.000 | 6.1192-002 | 5.1721-003 | 5.1653-003 | 0.13  |
| 1  | 150.000 | 9.5478-002 | 7.8184-003 | 7.8043-003 | 0.18  |
| 1  | 155.000 | 1.4426-001 | 1.1464-002 | 1.1436-002 | 0.24  |
| 1  | 160.000 | 2.1176-001 | 1.6358-002 | 1.6308-002 | 0.31  |
| 1  | 165.000 | 3.0288-001 | 2.2781-002 | 2.2694-002 | 0.38  |
| 1  | 170.000 | 4.2317-001 | 3.1042-002 | 3.0899-002 | 0.46  |
| 1  | 175.000 | 5.7882-001 | 4.1479-002 | 4.1252-002 | 0.55  |
| 1  | 180.000 | 7.7662-001 | 5.4457-002 | 5.4111-002 | 0.64  |
| 1  | 185.000 | 1.0239+000 | 7.0359-002 | 6.9860-002 | 0.73  |
| 1  | 190.000 | 1.3287+000 | 8.9635-002 | 8.8911-002 | 0.81  |
| 1  | 195.000 | 1.6991+000 | 1.1271-001 | 1.1171-001 | 0.89  |
| 1  | 200.000 | 2.1440+000 | 1.4006-001 | 1.3872-001 | 0.97  |
| 1  | 205.000 | 2.6726+000 | 1.7222-001 | 1.7047-001 | 1.03  |
| 1  | 210.000 | 3.2943+000 | 2.0973-001 | 2.0750-001 | 1.08  |
| 1  | 215.000 | 4.0186+000 | 2.5321-001 | 2.5043-001 | 1.11  |
| 1  | 220.000 | 4.8561+000 | 3.0331-001 | 2.9993-001 | 1.13  |
| 1  | 225.000 | 5.6165+000 | 3.6077-001 | 3.5674-001 | 1.13  |
| 1  | 230.000 | 6.9105+000 | 4.2642-001 | 4.2173-001 | 1.11  |
| 1  | 235.000 | 8.1487+000 | 5.0120-001 | 4.9585-001 | 1.08  |
| 1  | 240.000 | 9.5420+000 | 5.8618-001 | 5.8025-001 | 1.02  |
| 1  | 245.000 | 1.1102+001 | 6.8262-001 | 6.7626-001 | 0.94  |
| 1  | 250.000 | 1.2839+001 | 7.9203-001 | 7.8551-001 | 0.83  |
| 1  | 255.000 | 1.4766+001 | 9.1618-001 | 9.0997-001 | 0.68  |
| 1  | 260.000 | 1.6895+001 | 1.0572+000 | 1.0522+000 | 0.48  |
| 1  | 265.000 | 1.9238+001 | 1.2179+000 | 1.2154+000 | 0.21  |
| 1  | 270.000 | 2.1810+001 | 1.4016+000 | 1.4041+000 | -0.18 |
| 1  | 275.000 | 2.4624+001 | 1.6125+000 | 1.6245+000 | -0.74 |
| 1  | 280.000 | 2.7697+001 | 1.8563+000 | 1.8861+000 | -1.58 |
| 1  | 285.000 | 3.1047+001 | 2.1404+000 | 2.2047+000 | -2.91 |
| 1  | 290.000 | 3.4693+001 | 2.4754+000 | 2.6108+000 | -5.19 |

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## PROGRAM VIRUS

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C   ETHANE VIRIAL COEFFICIENTS,    X = T/TCRT,  Q = X**1/2,
C   BV = (B1 + B2/X**EB + B3/X + B4/X2 + B5/X3)*(1-(TZ/T)**1/4).
C   CV = (C1/X**EC + C2/X3 + C3/X5)*(1-TZ/T).
C   I), (1)EUCKEN, (2)LAMBERT, (3)MICHELS, (4)HOOVER, (5)POPE,
C   (6)MCGLASHAN, (7)CHUEH, (8)GUNN, (10)DOUSLIN, PREPRINT.
C   VCRT, CC/MOL, ROSSINI(1953)/MCGLASHAM=148, EUBANK/POPE=146.2,
C   TESTER(1961)=141.7, DOUSLIN(1973)=145.56.
      COMMON/1/4,EB,EC,TZB,TZC, BVS,CVS, B(5),C(4)
      COMMON/3/ DPSDT
      COMMON/999/NP,NF,H(15),Y(200),G(200,15)
      DIMENSION ID(200),T(200),BV(200),CV(200),X(200),XQ(200)
1   FORMAT(I5, 2F10.0)
2   FORMAT(1H1 13X 1HM 5X54E(BC) 8X2HTZ 8X2HSS)
3   FORMAT(10X I5, 2F10.3, F10.4)
4   FORMAT(1H1 17X *ETHANE SECOND VIRIAL COEFFICIENT*//
      1 18X4HEB =F6.3, 5H, TZ =F6.1// 15X 5F12.6//
      2 18X2HID 7X3HT,K 5X4HT/TC 7X2HB* 5X4HCALC 5X4HDIFF 5X4HPCNT)
5   FORMAT(15X I5, F10.3, F9.4, 3F9.3, F9.2)
6   FORMAT(1H117X*THIRD VIRIAL, M=*I2, 6H, EC =F6.3// 16X F10.3,
      1 4F11.6// 18X2HID 7X3HT,K 4X6HT/TCRT 8X24C* 5X5HCALCD 6X4HDIFF )
7   FORMAT(15X I5, F10.3, F10.4, 3F10.3)
8   FORMAT(18X 4HNP =I3, 12H, MEANDIFF = F7.3)
9   FORMAT(18X 4HNP =I3, 11H, MEANPCT =F6.3)
10  FORMAT(1H1 15X*TERMS OF THE VIRIAL EQUATION FOR SATURATED VAPOR*//
      1 17X3HT,K 7X5HP,ATM 7X5HMOL/L 5X5HDI/DN
      2 7X3HB*S 6X4HC*S2 4X6HZ(T,D) )
11  FORMAT(10X F10.0, 2F12.7, 4F10.6)
12  FORMAT(1H1 17X 24ID 7X3HT,K 5X4HT/TC 7X2HB* 5X4HCALC
      1 5X4HDIFF 5X4HPCNT)
13  FORMAT(1H117X2HID 7X3HT,K 4X6HT/TCRT 8X2HC* 5X5HCALCD 6X4HDIFF)
15  TTR2=89.899 $ TCRT=305.33 $ DCRT=1.0/145.56
C   GENERATE MCGLASHAM DATA FOR BV(T), CC/MOL.
C   INCREASE ABS(MCGLASHAM) BY ONE PERCENT (148/145.56 = 1.017).
16  N=0 $ DO 19 J=1,12 $ N = N+1 $ TT = T(N) = 140 + 10*J
17  X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N)) $ ID(N) = 6
18  BV(N) = 1.01*GLABF(TT) $ Y(N) = BV(N)*DCRT
19  CONTINUE
C   READ DOUSLIN(1973) DATA, CC/MOL.
20  DO 23 J=1,99 $ READ 1, IDD,TT,88 $ IF(IDD) 21,24
21  N = N+1 $ ID(N)=IDD $ T(N)=TT $ BV(N)=88
22  X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N)) $ Y(N)=88*DCRT
23  CONTINUE
24  NP = N $ NF = 5 $ SSK = 1.0E+010
C   READ SECOND VIRIAL DATA.
25  DO 28 J=1,99 $ READ 1, IDD,TT,88 $ IF(IDD) 26,29
26  N = N+1 $ ID(N)=IDD $ T(N)=TT $ BV(N)=88
27  X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N)) $ Y(N)=88*DCRT
28  CONTINUE
29  NPP = N $ M = 0
C   EXPLORE VALUES FOR EB AND FOR TZB.
C   MCGLASHAM TZB NEAR 2.7*TCRT = 824 K.
30  EB = 0.25 $ TZ = TZB = 740 $ PRINT 2
C   31 DO 34 IE=1,3 $ EB = 0.25*IE
C   32 DO 34 IT=1,17 $ TZ = 640 + 10*IT

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## SUBJECT

Ethane Virial Coefficients and Saturated Vapor Densities

NAME

R. D. Goodwin

DATE

August 14, 1973

```

33 DO 36 J=1,NP $ U=X(J) $ Q=XQ(J) $ W = 1-(TZ/T(J))**0.25
34 G(J,1)=W $ G(J,2)=W/U**EB $ G(J,3)=W/U $ G(J,4)=W/U**2
35 G(J,5)=W/U**3
36 CONTINUE $ CALL EGENFT $ SS = 0
37 DO 39 J=1,NP $ YC = 0 $ DO 38 K=1,NF
38 YC = YC + H(K)*G(J,K)
39 SS = SS + ABSF(Y(J)/YC-1) $ SS = 100*SS/NP
40 IF(SS.LT.SSK) 41,44
41 SSK=SS $ EK=EB $ TK=TZ $ DO 42 K=1,5
42 B(K) = H(K)
44 PRINT 3, M,EB,TZ,SS $ EB=EK $ TZ=TZB=TK $ SS = 0
C   JSE SAVED CONSTANTS FOR DEVIATIONS.
45 PRINT 4, EB, TZ, (B(K),K=1,5)
46 DO 51 J=1,NPP $ U=X(J) $ Q=XQ(J) $ W = 1-(TZ/T(J))**0.25
47 YC = W*(B(1) + B(2)/U**EB + B(3)/U + B(4)/U**2 + B(5)/U**3)
48 DIF=Y(J)-YC $ PCT=-100*DIF/YC $ SS=SS+ABSF(PCT)
49 PRINT 5, ID(J),T(J),X(J),Y(J),YC,DIF,PCT $ IF(J-NP) 51,50
50 SS = SS/NP $ PRINT 9, NP,SS $ PRINT 12
51 CONTINUE $ N = 0
C   GENERATE THIRD VIRIAL DATA VIA CHUEH(1967), ID = 7.
C   DIMINISH CHUEH DATA BY 2 PERCENT.
52 DO 55 J=1,6 $ N = N+1 $ TT = T(N) = 200 + 10*J
53 X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N)) $ ID(N) = 7
54 CV(N) = 0.98*CHUCF(TT) $ Y(N) = CV(N)*DCRT**2
55 CONTINUE $ K = N + 1
C   READ DOUSLIN(1973) DATA, (CC/MOL)**2.
56 DO 58 J=K,99 $ READ 1, ID(J),T(J),CV(J) $ IF(ID(J)) 57,59
57 X(J)=T(J)/TCRT $ XQ(J)=SQRTF(X(J)) $ Y(J)=CV(J)*DCRT**2
58 CONTINUE
59 NP = J-1 $ NF = 3 $ SSK = 1.0E+010
C   READ THIRD VIRIAL DATA. TZC NEAR 220 K.
60 K = NP+1 $ DO 63 J=K,99
61 READ 1, ID(J),T(J),CV(J) $ IF(ID(J)) 62,64
62 X(J) = T(J)/TCRT $ XQ(J)=SQRTF(X(J)) $ Y(J)=CV(J)*DCRT**2
63 CONTINUE
64 NPP = J-1 $ EC = 1.0 $ PRINT 2
C   EXPLORE VALUES FOR EC AND FOR TZ.
C   65 DO 76 IE=1,4 $ EC = 0.5*IE
66 DO 76 IT=1,11 $ TZ = 217.60 + 0.05*IT
67 DO 59 J=1,NP $ U = X(J) $ W = 1-TZ/T(J)
68 G(J,1)=W/U**EC $ G(J,2)=W/U**3 $ G(J,3)=W/U**5
69 CONTINUE $ CALL EGENFT $ SS = 0
70 DO 72 J=1,NP $ YC = 0 $ DO 71 K=1,NF
71 YC = YC + H(K)*G(J,K)
72 SS = SS + ABSF(Y(J)-YC) $ SS = SS/NP
73 IF(SS.LT.SSK) 74,76
74 SSK=SS $ TK=TZ $ EK=EC $ MK=M $ DO 75 K=1,4
75 C(K) = H(K)
76 PRINT 3, M,EC,TZ,SS $ M = MK
77 TZC = TZ = TK $ EC = EK $ SS = 0
C   USE SAVED CONSTANTS FOR DEVIATIONS.
79 PRINT 6, M,EC,TZ, (C(K),K=1,4)
80 DO 85 J=1,NPP $ U = X(J) $ W = 1-TZ/T(J)
81 YC = W*(C(1)/U**EC + C(2)/U**3 + C(3)/U**5)
82 PCT = Y(J)-YC $ SS = SS + ABSF(PCT)

```

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## SUBJECT

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```

83 PRINT 7, ID(J),T(J),X(J),Y(J),YC,PCT $ IF(J-NP) 85,84
84 SS = SS/NP $ PRINT 8, NP,SS $ PRINT 13
85 CONTINUE
C   NOW EXAMINE TERMS OF THE VIRIAL EQUATION AT SATURATION.
C   THE IDEAL GAS DENSITY IS DI = P/(R*T),
90 PRINT 10 $ DO 95 J=1,44 $ TT = 85 + 5*J
91 PS=PSATF(TT) $ DN=DNGSF(TT) $ Z = ZIPF(TT,DN)
92 DI = PS/TT/0.082056156 $ DR = DI/DN
95 PRINT 11, TT,PS,DN, DR, BVS,CVS, Z
99 STOP $ END

```

SINGLE-BANK COMPILATION.

## FUNCTION CHUCF(T)

```

C   ETHANE THIRD VIRIAL VIA CHUEH FORMULA(1967), (CC/MOL)**2.
C   CV(T)/VCRT**2 = FA*FB + FC, FA = A/Q + B/X5,
C   FB = 1 - EXP(1-AL*X2), FC = EXP(-C + D*X - E*X2), X = T/TCRT.
DATA (TCRT=305.33), (VCRT=145.56), (AL=1.89)
DATA (A=0.232), (B=0.468), (C=2.49), (D=2.30), (E=2.70)
1 X=T/TCRT $ Q=SQRTF(SQRTF(X)) $ X2=X**2 $ X5=X**5
2 FA = A/Q + B/X5 $ FB = 1 - EXPF(1-AL*X2)
3 FC = EXPF(-C + D*X - E*X2)
4 CHUCF = (FA*FB+FC)*VCRT**2 $ RETURN $ END

```

## FUNCTION DNGSF(T)

```

C   PLANCK/KAMBEITZ VIA TESTER (P.171)/DIN. VALID 170 TO 305 K.
C   V = R*T/P - C1/X**A - C2*P**2/X**B, X = T/100,
C   V IN CC/GRAM, T IN KELVINS, P IN KG/CM**2,
C   1 AT1 = 1.03323 KG/CM**2, R=2.822, C1=69.0, C2=27.9, A=2.4, B=9.0
DATA (R=2.822), (C1=69.0), (C2=27.9), (A=2.4), (B=9.0), (WM=30.07)
1 P = PSATF(T) $ P = 1.03323*P $ P2 = P**2
2 X = T/100 $ XA = X**A $ XB = X**B
3 V = R*T/P - C1/XA - C2*P2/XB
4 DNGSF = 1000.88/V/WM $ RETURN $ END

```

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## SUBJECT

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## FUNCTION GLABF(T)

```

C ETHANE SECOND VIRIAL COEFF. VIA MC GLASHAM FORMULA (1962).
C MC G. BELIEVES EUCKEN/PARTS ARE WRONG.
C  $3V(T)/VCRT = B1 - B2/X - B3/X^2 - B4/X^{4.5}$ ,  $X = T/TCRT$ .
  DATA (TCRT=305.4), (VCRT=148.0)
  DATA (B1=0.430), (B2=0.886), (B3=0.694), (B4=0.0375)
1  $X=T/TCRT$   $X2=X^2$   $X4=X^{4.5}$ 
2  $F = B1 - B2/X - B3/X^2 - B4/X^N$ 
9 GLABF = VCRT*F  $\$$  RETURN  $\$$  END

```

07/26/73

## FUNCTION PSATF(T)

```

C LN(P/PTRP) = A*X + B*X^2 + C*X^3 + D*X^4 + E*X*(1-X)**EP.
  COMMON/3/ DPSOT
  DATA (TTRP=89.899), (TCRT=305.33), (PTRP=9.616E-6), (EP=1.6)
  DATA (A=8.454987344), (B=12.488039775), (C=-4.104281551),
1 (D=-1.413860533), (E=8.526522526)
1 FORMAT(1H) 9X *PSATF = 0, T EXCEEDS TCRT. * / )
2  $XN=1-TTRP/TCRT$   $X=(1-TTRP/T)/XN$   $X2=X^2$   $X3=X^3$   $X4=X^4$ 
3  $DXDT = TTRP/XN/T^2$   $Q = 1-X$   $\$$  IF(Q) 4,5,6
4 PSATF = DPSOT = J  $\$$  PRINT 1  $\$$  RETURN
5 Z = Z1 = 0  $\$$  GO TO 7
6  $W = Q^{EP}$   $W1 = -EP*W/Q$   $Z = X*W$   $Z1 = W + X*W1$ 
7  $F = A*X + B*X^2 + C*X^3 + D*X^4 + E*Z$ 
8  $F1 = A + 2*B*X + 3*C*X^2 + 4*D*X^3 + E*Z1$ 
9 PSATF=PTRP*EXP(F)  $\$$  DPSOT=F1*PSATF*DXDT  $\$$  RETURN  $\$$  END

```

07/26/73

## FUNCTION ZIPF(T,J)

```

C  $Z(T,J) = 1 + BV(T)*S + 3V(T)*S^2$ ,  $S = D/DCRT$ ,  $X = T/TCRT$ .
C  $BV = (B1 + B2/X^{EB} + B3/X + B4/X^2 + B5/X^3)*(1-(TZ/T)^{1/4})$ .
C  $3V = (C1/X^{EC} + C2/X^3 + C3/X^5)*(1-TZ/T)$ .
  COMMON/1/M,EB,EC,TZB,TZC,BVS,CVS,B(5),C(4)
  DATA (TCRT=305.33), (VCRT=0.14556)
1  $S=D*VCRT$   $X=T/TCRT$   $Q=SQRT(X)$   $R=X^{EC}$ 
2  $X2=X^2$   $X3=X^3$   $X4=X^4$   $X5=X^5$ 
3  $ZB = 1 - (TZB/T)^{0.25}$   $ZC = 1 - TZC/T$ 
4  $BV = ZB*(B(1) + B(2)/X^{EB} + B(3)/X + B(4)/X^2 + B(5)/X^3)$ 
5  $CV = ZC*(C(1)/R + C(2)/X^3 + C(3)/X^5)$ 
6  $BVS = BV*S$   $CVS = CV*S^2$ 
7 ZIPF = 1 + BVS + CVS  $\$$  RETURN  $\$$  END

```



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## SUBJECT

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## PROGRAM VAPORDEN

```

C   ETHANE SATVAPORDEN VIA V.P. AND VIRIAL EQNS.
C   ON ISOTHERMS, ITERATE DEN IN VIRIAL EQN. TO MINIMIZE (P-PSAT).
    COMMON/3/ DPSOT
  1  FORMAT(13X *ETHANE SATD. VAPOR DENSITIES VIA V.P. AND VIRIAL EQNS.
  1  *///18X2HID 7X3HT,K 7X5HP,ATM 2X10HPLANK/KAMB 7X5HMOL/L 7X3HPCT)
  2  FORMAT(15X I5, F10.3, 3E12.4, F10.2)
  3  FORMAT(I5, F10.3, 2E15.5)
19  ID = 1  $  TTRP = 89.893  $  PRINT 1
20  DO 30 J=1,42  $  IF(J-1) 23,22
22  T = TTRP  $  GO TO 24
23  T = 30 + 5*J
24  DI = DNGSF(T)  $  P = PSATF(T)  $  DEN = FINDF(T,P,DI)
25  PUNCH 3, ID,T,DEN,P
27  DIF = DI-DEN  $  PCT = 100*DIF/DEN
29  PRINT 2, ID, T,P, DI,JEN, PCT
30  CONTINUE  $  STOP  $  END

```

SINGLE-BANK COMPILATION.

## FUNCTION FINDF(T,P,DI)

```

C   ON ISOTHERM T, ITERATE DEN TO MINIMIZE (P-PCALC).
    COMMON DZDS
    DATA (GK=0.082056156), (VCRT=0.14556)
  1  FORMAT(1H0 9X *FINDF = 0, FAILS TO CONVERGE.* / )
  2  D = DI  $  GT = GK*T  $  DO 9 J=1,50
  3  Z = ZIPF(T,D)  $  PC = D*GT*Z  $  DP = P-PC  $  AP = ABSF(DP)
  4  Q = AP/P-1.0E-6  $  IF(Q) 10,10,5
  5  DPDD = GT*(Z + D*DZDS*VCRT)  $  ADP = ABSF(DPDD)
  6  Q = AP/ADP/D-1.0E-6  $  IF(Q) 10,10,7
  7  D = D + DP/DPDD  $  IF(D) 8,8,9
  8  D = P/T/GK
  9  CONTINUE  $  FINDF = 0  $  PRINT 1  $  RETURN
10  FINDF = 0  $  RETURN  $  END

```

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SUBJECT

Ethane Virial Coefficients and Saturated Vapor Densities

NAME

R. D. Goodwin

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## FUNCTION DNGSF(T)

C PLANK/KAMREITZ VIA TESTER.

DATA (R=2.522), (C1=39.0), (C2=27.9), (A=2.4), (IB=9), (WM=30.07)

1 P = 1.03323\*PSATF(T) \$ P2 = P\*\*2

2 X = T/100 \$ XA = X\*\*A \$ XB = X\*\*IB

3 V = R\*T/P - C1/XA - C2\*P2/XB

4 DNGSF = 1000.88/V/WM \$ RETURN \$ END

08/01/73

## FUNCTION PSATF(T)

C LN(P/PTRP) = A\*X + B\*X2 + C\*X3 + D\*X4 + E\*X\*(1-X)\*\*EP.

COMMON/3/ DPSDT

C CONSTANTS VIA ZIEGLER TYPE B V.P. DATA.

DATA (TTRP=89.899), (TCRT=305.33), (PTRP=9.967E-6), (EP=1.5)

DATA (A=10.806922651), (B=8.344715938), (C=-3.119603823)

DATA (D=-0.642995191), (E=6.059966098)

1 FORMAT(1H0 9X \*PSATF = 0, T EXCEEDS TCRT. \* / )

2 XN=1-TTRP/TCRT \$ X=(1-TTRP/T)/XN \$ X2=X\*\*2 \$ X3=X\*\*3 \$ X4=X\*\*4

3 DXDT = TTRP/XN/T\*\*2 \$ Q = 1-X \$ IF(Q) 4,5,6

4 PSATF = DPSDT = 0 \$ PRINT 1 \$ RETURN

5 Z = Z1 = 0 \$ GO TO 7

6 W = Q\*\*EP \$ W1 = -EP\*W/Q \$ Z = X\*W \$ Z1 = W + X\*W1

7 F = A\*X + B\*X2 + C\*X3 + D\*X4 + E\*Z

8 F1 = A + 2\*B\*X + 3\*C\*X2 + 4\*D\*X3 + E\*Z1

9 PSATF=PTRP\*EXP(F) \$ DPSDT=F1\*PSATF\*DXDT \$ RETURN \$ END

## FUNCTION ZIPF(T,D)

C Z(T,D) = 1 + BV(X)\*S + CV(X)\*S\*\*2.

C BV = (B1 + B2/T + B3/X + B4/X2 + B5/X3)\*(1-(TZB/T)\*\*1/4).

C CV = (C1/X + C2/X3 + C3/X5)\*(1-TZC/T).

COMMON DZDS

DATA (TCRT=305.33), (VCRT=0.14556), (TZB=740.0), (TZC=217.8),

1 (B1=7.993156), (B2=-10.672497), (B3=9.217322), (B4=-2.481668),

2 (B5=0.342328), (C1=0.253773), (C2=0.865299), (C3=0.556075)

1 S=0\*VCRT \$ X=1/TCRT \$ Q=X\*\*0.25 \$ X2=X\*\*2 \$ X3=X\*\*3 \$ X5=X\*\*5

2 ZB = 1 - (TZB/T)\*\*0.25 \$ ZC = 1 - TZC/T

3 BV = ZB\*(B1 + B2/Q + B3/X + B4/X2 + B5/X3)

4 CV = ZC\*(C1/X + C2/X3 + C3/X5)

5 ZIPF = 1 + BV\*S + CV\*S\*\*2 \$ DZDS = BV + 2\*CV\*S

6 RETURN \$ END

## APPENDIX L

|                                                                                    |  |                               |          |      |
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| <b>LABORATORY NOTE</b>                                                             |  | 2750364                       | 73-5     | 1    |
| <b>SUBJECT</b><br>The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine |  | <b>NAME</b><br>R. D. Goodwin  |          |      |
|                                                                                    |  | <b>DATE</b><br>Sept. 18, 1973 |          |      |

1. Introduction.

These densities, and accurate analytical descriptions thereof, are essential for the computation of thermodynamic functions, in particular to obtain heats of vaporization via the Clapeyron equation, and to formulate the equation of state which originates on this locus [4].

We have had difficulties in representing the available ethane data, and therefore have returned to fundamentals. For comparison we shall include oxygen [18], fluorine [13], and methane [4]. Previous formulations occur in [4, 7]. We start with the saturated liquid densities because their representation is much simpler than that of the saturated vapor densities.

2. The Saturated Liquids.

It is well known that these densities are described near the critical point by the form

$$\rho = \rho_c + a \cdot (T_c - T) + b \cdot (T_c - T)^{\epsilon} \quad (1)$$

wherein the first two terms are the rectilinear diameter, and the exponent is near  $\epsilon = 0.35$ .

Let us constrain (1) at the boundaries by use of the variables,

$$x(T) \equiv (T_c - T)/(T_c - T_t), \quad (2)$$

$$W(\rho) \equiv (\rho - \rho_c)/(\rho_t - \rho_c), \quad (3)$$

where subscripts c and t refer to critical and triple points. Equation (1) now becomes,

$$W(\rho) = a \cdot x + b \cdot x^{\epsilon}, \quad (4)$$

and the constraint requires that  $a + b = 1$ . If we solve this for the constant b, we may expect to obtain a function  $Y(\rho, x)$  which is nearly constant over the entire range  $0 \leq x \leq 1$ ,

$$Y(\rho, x) \equiv [W(\rho) - x]/(x^{\epsilon} - x). \quad (5)$$

This sensitive function is useful for examining data.

In past work we found that three arbitrary coefficients are required to describe saturated liquid densities. We now find the following results via many exploratory computations. For the smoothed data used here for oxygen and fluorine, the use of five arbitrary coefficients gives an improvement in the "fit". For the rough experimental data used here for methane and ethane, the use of five arbitrary coefficients gives virtually no improvement in the "fit" as compared with only three coefficients. With only three, the first equation used was,

|                                                                  |  |                |          |      |
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$$Y(\rho, x) = A_1 + A_2 \cdot x + A_3 \cdot x^\alpha, \quad (6)$$

and we found exponent  $\alpha = 4/3$  for oxygen, fluorine and methane, but  $\alpha = 8/3$  for ethane. After much exploration we have selected the following representation,

$$Y(\rho, x) = A_1 + A_2 \cdot x^{2/3} + A_3 \cdot x \quad (7)$$

Table 1 gives the fixed-point constants. Table 2A gives the exponent  $\epsilon$  found by trial, the least-squares coefficients, the rms of relative density deviations in percent, and the number of datum pairs, NP.

Tables 3, 4, 5, 6 compare calculated with experimental densities. No temperature-scale adjustments have been made in present work. Column YX gives the experimental value of  $Y(\rho, x)$  via (5), whereas column YC gives the value calculated by the right side of (7). Table 7 compares ethane data not used for least squares.

Tables 8, 9, 10, 11 give saturated liquid densities computed by (7) at uniform temperatures, and also their slopes and curvatures.

The small deviations for oxygen and fluorine necessarily are systematic because the data were smoothed by the authors. The overall methane deviation is large because experimental data from various sources are included in the critical region.

The low-temperature ethane data of Miller were used to estimate the triple-point liquid density. Other data are from Canfield et al., and from Klosek/McKinley. The high-temperature "data" of Eubank are a correlation of available experimental data down to the boiling point 184.5 K, ( $x = 0.561$ ). We estimate uncertainty in our calculation of these densities to be about 0.1 percent over the entire range.

Concerning assignment of critical densities, we at first found both  $\rho_c$  and exponent  $\epsilon$  simultaneously by trial to minimize the overall deviation. The results are rough because these two parameters are mutually compensating for data in the critical region. Hence we have adjusted  $\rho_c$  one step at a time for both saturated liquid and saturated vapor, examining the values of  $\epsilon$  found by trial. We select that value of  $\rho_c$  which yields reasonable exponents  $\epsilon$  for both liquid and vapor. For methane it thus is necessary to select  $\rho_c = 10.2$  mol/l, at the upper limit of uncertainty in the experimental values [4].

### 3. The Saturated Vapors

Densities of the ethane vapors range thru a factor of about  $10^6$ . We have given reasons for using the logarithm of vapor densities, with arguments in powers of  $(1/T)$ , [7]. Define the normalized variables

$$z(T) \equiv (T_c/T - 1)/(T_c/T_t - 1), \quad (8)$$

$$W(\rho) \equiv \ln(\rho_c/\rho)/\ln(\rho_c/\rho_t). \quad (9)$$



|                                                                  |  |                |          |      |
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We write the vapor densities equation for the critical region as follows,

$$-W(\rho) = (b-1) \cdot z - b \cdot z^e \quad (10)$$

wherein the minus sign on the left arises merely from our definition of  $W(\rho)$ . Solving (10) for  $b$  yields the dependent variable,

$$Y(\rho, z) \equiv [W(\rho) - z] / (z^e - z) . \quad (11)$$

For the present work we have explored all kinds of representations, finally selecting the expression,

$$Y(\rho, z) = A_1 + \sum_{i=2}^5 A_i \cdot z^{i/3} . \quad (12)$$

Table 2B gives results for (12), analagous to table 2A for the liquid. Tables 12, 13, 14, 15 compare calculated with experimental vapor densities. Column YX is the experimental value of  $Y(\rho, z)$  via (11), whereas YC is calculated by the right side of (12). Table 16 compares ethane data not used for least squares. Tables 17, 18, 19, 20 give uniformly computed densities and derivatives via (12).

Computer programs used in this work are attached as an appendix.

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| SUBJECT<br>The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine |                                                                                                                                                                                         | NAME R. D. Goodwin  |          |      |
|                                                                             |                                                                                                                                                                                         | DATE Sept. 18, 1973 |          |      |
| 4. Bibliography                                                             |                                                                                                                                                                                         |                     |          |      |
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| [2]                                                                         | D. R. Douslin and R. H. Harrison, Pressure-volume-temperature relations for ethane, (U.S. Bureau of Mines, Bartlesville, Okla. 74003, Manuscript for J. Chem. Thermodynamics, 1973).    |                     |          |      |
| [3]                                                                         | P. T. Eubank, Thermodynamic properties of ethane: vapor-liquid coexistence, Advances in Cryogenic Engineering <u>17</u> , 270 (Plenum Pub. Corp., New York, N.Y. 10011, 1971).          |                     |          |      |
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|                                                                  |                                                                                                                                                                                                                                     |                |          |      |
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|                                                                  |                                                                                                                                                                                                                                     | DATE           |          |      |
|                                                                  |                                                                                                                                                                                                                                     | Sept. 18, 1973 |          |      |
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List of Authors for Computer Tables

| <u>ID*</u> | <u>Author(s)</u>        | <u>Reference</u> |
|------------|-------------------------|------------------|
| 1          | Goodwin (Virial + V.P.) | [6]              |
| 6          | Porter                  | [12]             |
| 9          | Tester                  | [16]             |
| 10         | Douslin                 | [2]              |
| 11         | Sliwinski               | [15]             |
| 12         | Canfield et al.         | [1, 14]          |
| 13         | Klosek                  | [9]              |
| 14         | Miller                  | [11]             |
| 15         | Eubank                  | [3]              |
| 16         | Tomlinson               | [17]             |
| 98         | Prydz                   | [13]             |
| 99         | Weber                   | [18]             |

\* For METHANE, see references in [4].



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Table 1. The fixed-point constants.

|                   | <u>Oxygen</u>           | <u>Fluorine</u>       | <u>Methane</u>           | <u>Ethane</u>           |
|-------------------|-------------------------|-----------------------|--------------------------|-------------------------|
| $T_t$ , K         | 54.3507                 | 53.4811               | 90.680                   | 89.899                  |
| $T_c$ , K         | 154.576                 | 144.310               | 190.555                  | 305.330                 |
| $\rho_c$ , mol/l  | 13.63                   | 15.15                 | 10.20                    | 6.87                    |
| $\rho_t$ , liquid | 40.830                  | 44.8623               | 28.147                   | 21.680                  |
| $\rho_t$ , vapor  | $3.36122 \cdot 10^{-4}$ | $5.670 \cdot 10^{-4}$ | $1.567865 \cdot 10^{-2}$ | $1.35114 \cdot 10^{-6}$ |

Table 2A. Constants for liquid equation (7)

|            | <u>Oxygen</u> | <u>Fluorine</u> | <u>Methane</u> | <u>Ethane</u> |
|------------|---------------|-----------------|----------------|---------------|
| $\epsilon$ | 0.349         | 0.354           | 0.361          | 0.350         |
| $A_1$      | 0.758 8805    | 0.791 3438      | 0.837 0910     | 0.761 7350    |
| $A_2$      | 0.228 3200    | 0.112 9132      | 0.084 1613     | 0.298 6535    |
| $A_3$      | -0.230 4342   | -0.100 6980     | -0.074 7858    | -0.327 6239   |
| rms, %     | 0.014         | 0.010           | 0.084          | 0.142         |
| NP         | 50            | 46              | 49             | 29            |

Table 2B. Constants for vapor equation (12)

|            | <u>Oxygen</u> | <u>Fluorine</u> | <u>Methane</u> | <u>Ethane</u> |
|------------|---------------|-----------------|----------------|---------------|
| $\epsilon$ | 0.382         | 0.362           | 0.382          | 0.362         |
| $A_1$      | 0.277 3707    | 0.257 1572      | 0.374 1014     | 0.192 7743    |
| $A_2$      | -0.338 6621   | -0.227 0644     | -0.261 5731    | 0.041 5501    |
| $A_3$      | 0.769 0708    | 0.605 3864      | 0.675 3322     | -0.789 2263   |
| $A_4$      | -1.576 1185   | -1.391 6332     | -1.012 2063    | 0.357 6675    |
| $A_5$      | 0.939 8713    | 0.792 5719      | 0.439 8834     | 0.124 5438    |
| rms, %     | 0.052         | 0.134           | 0.148          | 0.104         |
| NP         | 50            | 46              | 96             | 29            |

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Table 3. Comparison of oxygen liquid densities.

TCRT = 154.576, TTRP = 54.3507

OCRT = 13.630, DTRP = 40.8300

E = 0.349

7.5888052-001 2.2832003-001 -2.3043415-001

0.0000000+000 0.0000000+000 0.0000000+000

| ID | T,K     | MOL/L  | CALC   | PCNT  | X       | YX      | YC      | YDIF     |
|----|---------|--------|--------|-------|---------|---------|---------|----------|
| 99 | 56.000  | 40.601 | 40.603 | -0.00 | 0.98354 | 0.75202 | 0.75805 | -0.00603 |
| 99 | 58.000  | 40.323 | 40.326 | -0.01 | 0.96359 | 0.75397 | 0.75958 | -0.00561 |
| 99 | 60.000  | 40.048 | 40.049 | -0.00 | 0.94363 | 0.76038 | 0.76109 | -0.00072 |
| 99 | 62.000  | 39.777 | 39.770 | 0.02  | 0.92368 | 0.76779 | 0.76258 | 0.00520  |
| 99 | 64.000  | 39.494 | 39.491 | 0.01  | 0.90372 | 0.76630 | 0.76405 | 0.00225  |
| 99 | 66.000  | 39.216 | 39.210 | 0.01  | 0.88377 | 0.76840 | 0.76550 | 0.00291  |
| 99 | 68.000  | 38.926 | 38.928 | -0.00 | 0.86381 | 0.76610 | 0.76692 | -0.00081 |
| 99 | 70.000  | 38.655 | 38.644 | 0.03  | 0.84386 | 0.77243 | 0.76831 | 0.00411  |
| 99 | 72.000  | 38.358 | 38.358 | -0.00 | 0.82390 | 0.76966 | 0.76969 | -0.00002 |
| 99 | 74.000  | 38.081 | 38.071 | 0.03  | 0.80395 | 0.77392 | 0.77103 | 0.00289  |
| 99 | 76.000  | 37.779 | 37.782 | -0.01 | 0.78399 | 0.77145 | 0.77235 | -0.00090 |
| 99 | 78.000  | 37.495 | 37.491 | 0.01  | 0.76404 | 0.77482 | 0.77364 | 0.00118  |
| 99 | 80.000  | 37.202 | 37.197 | 0.01  | 0.74408 | 0.77614 | 0.77490 | 0.00124  |
| 99 | 82.000  | 36.900 | 36.901 | -0.00 | 0.72413 | 0.77539 | 0.77613 | -0.00014 |
| 99 | 84.000  | 36.603 | 36.602 | 0.00  | 0.70417 | 0.77750 | 0.77733 | 0.00017  |
| 99 | 86.000  | 36.298 | 36.301 | -0.01 | 0.68422 | 0.77788 | 0.77950 | -0.00061 |
| 99 | 88.000  | 35.997 | 35.996 | 0.00  | 0.66426 | 0.77979 | 0.77963 | 0.00016  |
| 99 | 90.000  | 35.689 | 35.688 | 0.00  | 0.64431 | 0.78081 | 0.78073 | 0.00007  |
| 99 | 92.000  | 35.373 | 35.377 | -0.01 | 0.62435 | 0.78118 | 0.78180 | -0.00061 |
| 99 | 94.000  | 35.063 | 35.062 | 0.00  | 0.60440 | 0.78305 | 0.78282 | 0.00023  |
| 99 | 96.000  | 34.734 | 34.742 | -0.02 | 0.58444 | 0.78261 | 0.78381 | -0.00120 |
| 99 | 98.000  | 34.412 | 34.418 | -0.02 | 0.56449 | 0.78376 | 0.78475 | -0.00099 |
| 99 | 100.000 | 34.083 | 34.090 | -0.02 | 0.54453 | 0.78472 | 0.78565 | -0.00093 |
| 99 | 102.000 | 33.750 | 33.756 | -0.02 | 0.52458 | 0.78563 | 0.78651 | -0.00088 |
| 99 | 104.000 | 33.411 | 33.417 | -0.02 | 0.50462 | 0.78653 | 0.78732 | -0.00072 |
| 99 | 106.000 | 33.069 | 33.072 | -0.01 | 0.48467 | 0.78772 | 0.78807 | -0.00035 |
| 99 | 108.000 | 32.712 | 32.720 | -0.02 | 0.46471 | 0.78870 | 0.78878 | -0.00008 |
| 99 | 110.000 | 32.362 | 32.361 | 0.00  | 0.44476 | 0.78960 | 0.78943 | 0.00017  |
| 99 | 112.000 | 31.990 | 31.995 | -0.02 | 0.42480 | 0.78946 | 0.79101 | -0.00056 |
| 99 | 114.000 | 31.616 | 31.620 | -0.01 | 0.40485 | 0.79005 | 0.79054 | -0.00049 |
| 99 | 116.000 | 31.236 | 31.236 | -0.02 | 0.38489 | 0.79038 | 0.79100 | -0.00062 |
| 99 | 118.000 | 30.845 | 30.842 | 0.01  | 0.36494 | 0.79169 | 0.79138 | 0.00031  |
| 99 | 120.000 | 30.441 | 30.438 | 0.01  | 0.34498 | 0.79203 | 0.79169 | 0.00039  |
| 99 | 122.000 | 30.021 | 30.021 | -0.00 | 0.32503 | 0.79190 | 0.79192 | -0.00001 |
| 99 | 124.000 | 29.595 | 29.591 | 0.01  | 0.30507 | 0.79239 | 0.79205 | 0.00034  |
| 99 | 126.000 | 29.146 | 29.147 | -0.00 | 0.28512 | 0.79203 | 0.79209 | -0.00006 |
| 99 | 128.000 | 28.686 | 28.685 | 0.00  | 0.26516 | 0.79210 | 0.79201 | 0.00008  |
| 99 | 130.000 | 28.209 | 28.205 | 0.01  | 0.24521 | 0.79216 | 0.79182 | 0.00033  |
| 99 | 132.000 | 27.709 | 27.704 | 0.02  | 0.22525 | 0.79192 | 0.79150 | 0.00042  |
| 99 | 134.000 | 27.181 | 27.179 | 0.01  | 0.20530 | 0.79129 | 0.79103 | 0.00026  |
| 99 | 136.000 | 26.631 | 26.625 | 0.02  | 0.18534 | 0.79103 | 0.79039 | 0.00063  |
| 99 | 138.000 | 26.042 | 26.037 | 0.02  | 0.16539 | 0.78999 | 0.78956 | 0.00043  |
| 99 | 140.000 | 25.413 | 25.410 | 0.01  | 0.14543 | 0.78883 | 0.78851 | 0.00032  |
| 99 | 142.000 | 24.734 | 24.733 | 0.01  | 0.12548 | 0.78733 | 0.78719 | 0.00014  |
| 99 | 144.000 | 23.992 | 23.993 | -0.00 | 0.10552 | 0.78549 | 0.78555 | -0.00006 |
| 99 | 146.000 | 23.164 | 23.170 | -0.02 | 0.08557 | 0.78287 | 0.78350 | -0.00063 |
| 99 | 148.000 | 22.227 | 22.230 | -0.01 | 0.06561 | 0.78057 | 0.78090 | -0.00033 |
| 99 | 150.000 | 21.106 | 21.108 | -0.01 | 0.04566 | 0.77724 | 0.77753 | -0.00029 |
| 99 | 152.000 | 19.646 | 19.647 | -0.00 | 0.02570 | 0.77280 | 0.77284 | -0.00004 |
| 99 | 154.000 | 17.106 | 17.104 | 0.01  | 0.00575 | 0.76528 | 0.76488 | 0.00040  |

NP = 50, RHSPCT = 0.014

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## SUBJECT

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Table 4. Comparison of fluorine liquid densities.

$$E = 0.354$$

$$TCRT = 144.310, TTRP = 53.4811$$

$$DCRT = 15.150, DTRP = 44.8623$$

$$7.9134383-001 \quad 1.1291315-001 \quad -1.0069804-001$$

$$0.0000000+000 \quad 0.0000000+000 \quad 0.0000000+000$$

| ID | T,K     | MOL/L  | CALC   | PCNT  | X       | YX      | YC      | YDIF     |
|----|---------|--------|--------|-------|---------|---------|---------|----------|
| 98 | 54.000  | 44.781 | 44.781 | 0.00  | 0.99429 | 0.80556 | 0.80370 | 0.00186  |
| 98 | 56.000  | 44.465 | 44.464 | 0.00  | 0.97227 | 0.80524 | 0.80425 | 0.00099  |
| 98 | 58.000  | 44.146 | 44.146 | 0.00  | 0.95025 | 0.80550 | 0.80479 | 0.00071  |
| 98 | 60.000  | 43.825 | 43.825 | 0.00  | 0.92823 | 0.80574 | 0.80532 | 0.00042  |
| 98 | 62.000  | 43.501 | 43.501 | 0.00  | 0.90621 | 0.80603 | 0.80583 | 0.00021  |
| 98 | 64.000  | 43.174 | 43.174 | -0.00 | 0.88419 | 0.80632 | 0.80633 | -0.00000 |
| 98 | 66.000  | 42.845 | 42.845 | -0.00 | 0.86217 | 0.80662 | 0.80681 | -0.00019 |
| 98 | 68.000  | 42.512 | 42.513 | -0.00 | 0.84015 | 0.80693 | 0.80728 | -0.00034 |
| 98 | 70.000  | 42.176 | 42.177 | -0.00 | 0.81813 | 0.80728 | 0.80773 | -0.00045 |
| 98 | 72.000  | 41.836 | 41.838 | -0.01 | 0.79611 | 0.80760 | 0.80817 | -0.00056 |
| 98 | 74.000  | 41.493 | 41.496 | -0.01 | 0.77409 | 0.80796 | 0.80859 | -0.00063 |
| 98 | 76.000  | 41.146 | 41.149 | -0.01 | 0.75207 | 0.80831 | 0.80899 | -0.00068 |
| 98 | 78.000  | 40.795 | 40.799 | -0.01 | 0.73005 | 0.80863 | 0.80938 | -0.00069 |
| 98 | 80.000  | 40.440 | 40.444 | -0.01 | 0.70803 | 0.80903 | 0.80974 | -0.00071 |
| 98 | 82.000  | 40.081 | 40.085 | -0.01 | 0.68602 | 0.80941 | 0.81009 | -0.00068 |
| 98 | 84.000  | 39.717 | 39.720 | -0.01 | 0.66400 | 0.80977 | 0.81042 | -0.00065 |
| 98 | 86.000  | 39.347 | 39.351 | -0.01 | 0.64198 | 0.81011 | 0.81073 | -0.00061 |
| 98 | 88.000  | 38.973 | 38.976 | -0.01 | 0.61996 | 0.81047 | 0.81101 | -0.00054 |
| 98 | 90.000  | 38.592 | 38.596 | -0.01 | 0.59794 | 0.81080 | 0.81127 | -0.00047 |
| 98 | 92.000  | 38.206 | 38.209 | -0.01 | 0.57592 | 0.81112 | 0.81151 | -0.00039 |
| 98 | 94.000  | 37.813 | 37.815 | -0.01 | 0.55390 | 0.81143 | 0.81172 | -0.00029 |
| 98 | 96.000  | 37.413 | 37.415 | -0.00 | 0.53188 | 0.81171 | 0.81191 | -0.00019 |
| 98 | 98.000  | 37.005 | 37.006 | -0.00 | 0.50986 | 0.81197 | 0.81206 | -0.00009 |
| 98 | 100.000 | 36.590 | 36.590 | 0.00  | 0.48784 | 0.81220 | 0.81219 | 0.00001  |
| 98 | 102.000 | 36.165 | 36.164 | 0.00  | 0.46582 | 0.81240 | 0.81229 | 0.00012  |
| 98 | 104.000 | 35.731 | 35.729 | 0.01  | 0.44380 | 0.81256 | 0.81235 | 0.00021  |
| 98 | 106.000 | 35.286 | 35.283 | 0.01  | 0.42178 | 0.81268 | 0.81238 | 0.00030  |
| 98 | 108.000 | 34.829 | 34.826 | 0.01  | 0.39976 | 0.81274 | 0.81236 | 0.00038  |
| 98 | 110.000 | 34.361 | 34.356 | 0.01  | 0.37774 | 0.81276 | 0.81231 | 0.00045  |
| 98 | 112.000 | 33.878 | 33.873 | 0.01  | 0.35572 | 0.81272 | 0.81221 | 0.00050  |
| 98 | 114.000 | 33.379 | 33.374 | 0.02  | 0.33370 | 0.81261 | 0.81206 | 0.00055  |
| 98 | 116.000 | 32.864 | 32.858 | 0.02  | 0.31168 | 0.81243 | 0.81186 | 0.00056  |
| 98 | 118.000 | 32.330 | 32.324 | 0.02  | 0.28967 | 0.81218 | 0.81161 | 0.00057  |
| 98 | 120.000 | 31.774 | 31.768 | 0.02  | 0.26765 | 0.81183 | 0.81129 | 0.00055  |
| 98 | 122.000 | 31.193 | 31.188 | 0.02  | 0.24563 | 0.81139 | 0.81090 | 0.00049  |
| 98 | 124.000 | 30.584 | 30.579 | 0.02  | 0.22361 | 0.81086 | 0.81042 | 0.00043  |
| 98 | 126.000 | 29.942 | 29.939 | 0.01  | 0.20159 | 0.81020 | 0.80986 | 0.00034  |
| 98 | 128.000 | 29.262 | 29.260 | 0.01  | 0.17957 | 0.80942 | 0.80920 | 0.00022  |
| 98 | 130.000 | 28.535 | 28.534 | 0.00  | 0.15755 | 0.80850 | 0.80842 | 0.00009  |
| 98 | 132.000 | 27.750 | 27.751 | -0.00 | 0.13553 | 0.80742 | 0.80749 | -0.00007 |
| 98 | 134.000 | 26.891 | 26.894 | -0.01 | 0.11351 | 0.80617 | 0.80638 | -0.00022 |
| 98 | 136.000 | 25.935 | 25.939 | -0.01 | 0.09149 | 0.80470 | 0.80506 | -0.00036 |
| 98 | 138.000 | 24.839 | 24.843 | -0.02 | 0.06947 | 0.80300 | 0.80343 | -0.00043 |
| 98 | 140.000 | 23.521 | 23.524 | -0.01 | 0.04745 | 0.80196 | 0.80137 | -0.00040 |
| 98 | 142.000 | 21.769 | 21.770 | -0.00 | 0.02543 | 0.79843 | 0.79855 | -0.00012 |
| 98 | 144.000 | 18.327 | 18.328 | -0.00 | 0.00341 | 0.79340 | 0.79356 | -0.00016 |

$$NP = 46, RMSPCT = 0.010$$



## LABORATORY NOTE

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## SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

## NAME

R.D. Goodwin

## DATE

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Table 5. Comparison of methane liquid densities.

$$E = 0.361$$

$$TCRT = -190.555, TTRP = 90.6800$$

$$DCRT = 10.200, DTRP = 28.1470$$

$$E = 0.361$$

$$8.3709103-001 \quad 8.4161267-002 \quad -7.4785753-002$$

$$0.0000000+000 \quad 0.0000000+000 \quad 0.0000000+000$$

| ID  | T,K     | MOL/L  | CALC   | PCNT  | X       | YX      | YC      | YDIF     |
|-----|---------|--------|--------|-------|---------|---------|---------|----------|
| 1   | 93.512  | 27.910 | 27.912 | -0.01 | 0.97164 | 0.84050 | 0.84699 | -0.00649 |
| 1   | 97.173  | 27.605 | 27.605 | 0.00  | 0.93499 | 0.84830 | 0.84764 | 0.00066  |
| 1   | 101.434 | 27.243 | 27.240 | 0.01  | 0.89233 | 0.85043 | 0.84836 | 0.00207  |
| 1   | 105.165 | 26.916 | 26.916 | 0.00  | 0.85497 | 0.84900 | 0.84896 | 0.00003  |
| 1   | 109.511 | 26.527 | 26.521 | 0.02  | 0.81045 | 0.85231 | 0.84964 | 0.00267  |
| 1   | 113.772 | 26.146 | 26.144 | 0.01  | 0.76879 | 0.85112 | 0.85023 | 0.00089  |
| 1   | 117.746 | 25.782 | 25.775 | 0.03  | 0.72900 | 0.85327 | 0.85074 | 0.00252  |
| 1   | 121.893 | 25.388 | 25.380 | 0.03  | 0.68748 | 0.85373 | 0.85123 | 0.00249  |
| 1   | 125.825 | 24.999 | 24.995 | 0.02  | 0.64811 | 0.85272 | 0.85165 | 0.00107  |
| 1   | 129.657 | 24.611 | 24.610 | 0.01  | 0.60974 | 0.85236 | 0.85201 | 0.00035  |
| 101 | 133.000 | 24.558 | 24.575 | -0.07 | 0.60631 | 0.84803 | 0.85204 | -0.00400 |
| 1   | 133.773 | 24.186 | 24.182 | 0.01  | 0.56853 | 0.85313 | 0.85233 | 0.00080  |
| 1   | 133.878 | 24.176 | 24.171 | 0.02  | 0.56748 | 0.85338 | 0.85234 | 0.00104  |
| 102 | 135.000 | 24.041 | 24.052 | -0.05 | 0.55625 | 0.85002 | 0.85242 | -0.00240 |
| 1   | 139.352 | 23.578 | 23.579 | -0.00 | 0.51267 | 0.85249 | 0.85266 | -0.00017 |
| 103 | 140.000 | 23.500 | 23.507 | -0.03 | 0.50618 | 0.85132 | 0.85269 | -0.00137 |
| 104 | 145.000 | 22.932 | 22.934 | -0.01 | 0.45612 | 0.85255 | 0.85285 | -0.00030 |
| 1   | 145.448 | 22.880 | 22.881 | -0.00 | 0.45163 | 0.85272 | 0.85286 | -0.00013 |
| 105 | 150.000 | 22.329 | 22.328 | 0.01  | 0.40606 | 0.85315 | 0.85287 | 0.00027  |
| 601 | 150.000 | 22.332 | 22.328 | 0.02  | 0.40606 | 0.85357 | 0.85287 | 0.00070  |
| 1   | 151.553 | 22.130 | 22.132 | -0.01 | 0.39051 | 0.85255 | 0.85285 | -0.00030 |
| 106 | 155.000 | 21.686 | 21.682 | 0.02  | 0.35599 | 0.85341 | 0.85274 | 0.00067  |
| 1   | 157.199 | 21.379 | 21.383 | -0.02 | 0.33398 | 0.85201 | 0.85263 | -0.00062 |
| 107 | 160.000 | 20.991 | 20.986 | 0.02  | 0.30593 | 0.85311 | 0.85242 | 0.00069  |
| 1   | 163.659 | 20.428 | 20.438 | -0.05 | 0.26930 | 0.85048 | 0.85205 | -0.00157 |
| 108 | 165.000 | 20.234 | 20.227 | 0.03  | 0.25587 | 0.85289 | 0.85188 | 0.00102  |
| 1   | 169.326 | 19.492 | 19.502 | -0.05 | 0.21256 | 0.84962 | 0.85117 | -0.00155 |
| 109 | 170.000 | 19.387 | 19.382 | 0.03  | 0.20581 | 0.85180 | 0.85104 | 0.00076  |
| 110 | 175.000 | 18.417 | 18.414 | 0.01  | 0.15574 | 0.85022 | 0.84981 | 0.00042  |
| 602 | 175.000 | 18.420 | 18.414 | 0.03  | 0.15574 | 0.85080 | 0.84981 | 0.00100  |
| 1   | 175.053 | 18.390 | 18.403 | -0.07 | 0.15521 | 0.84777 | 0.84979 | -0.00203 |
| 111 | 180.000 | 17.249 | 17.250 | -0.00 | 0.10568 | 0.84786 | 0.84800 | -0.00014 |
| 603 | 180.000 | 17.254 | 17.250 | 0.02  | 0.10568 | 0.84867 | 0.84800 | 0.00067  |
| 112 | 184.000 | 16.054 | 16.061 | -0.04 | 0.06563 | 0.84466 | 0.84588 | -0.00121 |
| 604 | 184.000 | 16.060 | 16.061 | -0.00 | 0.06563 | 0.84575 | 0.84588 | -0.00013 |
| 6   | 185.000 | 15.710 | 15.688 | 0.14  | 0.05532 | 0.84922 | 0.84517 | 0.00405  |
| 113 | 186.000 | 15.286 | 15.299 | -0.08 | 0.04561 | 0.84203 | 0.84442 | -0.00240 |
| 6   | 186.000 | 15.302 | 15.286 | 0.11  | 0.04530 | 0.84765 | 0.84440 | 0.00325  |
| 6   | 187.000 | 14.836 | 14.826 | 0.07  | 0.03528 | 0.84572 | 0.84351 | 0.00221  |
| 5   | 187.489 | 14.582 | 14.589 | -0.05 | 0.03070 | 0.84158 | 0.84305 | -0.00147 |
| 114 | 188.000 | 14.284 | 14.298 | -0.10 | 0.02558 | 0.83922 | 0.84248 | -0.00327 |
| 6   | 188.000 | 14.265 | 14.279 | 0.04  | 0.02527 | 0.84388 | 0.84245 | 0.00143  |
| 6   | 189.000 | 13.578 | 13.578 | 0.00  | 0.01525 | 0.84114 | 0.84113 | 0.00002  |
| 5   | 189.331 | 13.310 | 13.315 | -0.11 | 0.01226 | 0.83640 | 0.84065 | -0.00425 |
| 5   | 189.707 | 12.879 | 12.920 | -0.31 | 0.00649 | 0.83267 | 0.83996 | -0.01329 |
| 6   | 190.000 | 12.474 | 12.477 | -0.02 | 0.00524 | 0.83812 | 0.83924 | -0.00111 |
| 5   | 190.068 | 12.397 | 12.418 | -0.17 | 0.00488 | 0.83082 | 0.83915 | -0.00833 |
| 7   | 190.070 | 12.440 | 12.415 | 0.20  | 0.00486 | 0.84908 | 0.83914 | 0.00994  |
| 7   | 190.170 | 12.270 | 12.235 | 0.28  | 0.00385 | 0.85369 | 0.83887 | 0.01482  |

$$NP = 49, RMS PCT = 0.084$$

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Table 6. Comparison of ethane liquid densities.

ETHANE SATURATED LIQUID DENSITIES, E = 0.350

TCRT = 305.330, TTRP = 89.8990

DCRT = 6.870, DTRP = 21.6800

7.6173503-001 2.9865351-001 -3.2762394-001

3.0000000+000 0.0000000+000 0.0000000+000

| ID | T, K    | MOL/L  | CALC   | PCNT  | X       | YX      | YC      | YDIF     |
|----|---------|--------|--------|-------|---------|---------|---------|----------|
| 14 | 91.010  | 21.639 | 21.640 | -0.00 | 0.99484 | 0.72131 | 0.73343 | -0.01212 |
| 14 | 100.020 | 21.313 | 21.315 | -0.01 | 0.95302 | 0.73294 | 0.73873 | -0.00579 |
| 14 | 108.110 | 21.025 | 21.024 | 0.01  | 0.91547 | 0.74474 | 0.74338 | 0.00136  |
| 12 | 108.150 | 21.026 | 21.022 | 0.02  | 0.91528 | 0.74831 | 0.74341 | 0.00490  |
| 13 | 110.928 | 20.915 | 20.922 | -0.03 | 0.90239 | 0.73724 | 0.74498 | -0.00774 |
| 14 | 115.050 | 20.771 | 20.772 | -0.00 | 0.88325 | 0.74640 | 0.74729 | -0.00089 |
| 12 | 115.770 | 20.747 | 20.746 | 0.00  | 0.87991 | 0.74816 | 0.74769 | 0.00047  |
| 13 | 116.483 | 20.717 | 20.721 | -0.02 | 0.87660 | 0.74515 | 0.74809 | -0.00293 |
| 13 | 122.039 | 20.521 | 20.519 | 0.01  | 0.85081 | 0.75269 | 0.75115 | 0.00154  |
| 13 | 127.594 | 20.323 | 20.316 | 0.03  | 0.82503 | 0.75847 | 0.75415 | 0.00432  |
| 13 | 133.150 | 20.120 | 20.112 | 0.07  | 0.79924 | 0.76479 | 0.75709 | 0.00770  |
| 15 | 184.470 | 18.175 | 18.138 | 0.20  | 0.56101 | 0.79083 | 0.78108 | 0.00975  |
| 15 | 190.000 | 17.944 | 17.910 | 0.19  | 0.53535 | 0.79186 | 0.78325 | 0.00861  |
| 15 | 200.000 | 17.516 | 17.485 | 0.18  | 0.48893 | 0.79408 | 0.78690 | 0.00718  |
| 15 | 210.000 | 17.068 | 17.042 | 0.15  | 0.44251 | 0.79576 | 0.79019 | 0.00557  |
| 15 | 220.000 | 16.595 | 16.577 | 0.11  | 0.39609 | 0.79668 | 0.79304 | 0.00364  |
| 15 | 230.000 | 16.093 | 16.085 | 0.05  | 0.34967 | 0.79707 | 0.79541 | 0.00167  |
| 15 | 240.000 | 15.545 | 15.557 | -0.08 | 0.30325 | 0.79496 | 0.79719 | -0.00222 |
| 15 | 250.000 | 14.957 | 14.984 | -0.18 | 0.25683 | 0.79329 | 0.79826 | -0.00497 |
| 10 | 253.150 | 14.753 | 14.792 | -0.26 | 0.24221 | 0.79127 | 0.79843 | -0.00716 |
| 10 | 263.150 | 14.089 | 14.136 | -0.33 | 0.19579 | 0.78970 | 0.79829 | -0.00858 |
| 10 | 273.150 | 13.342 | 13.386 | -0.33 | 0.14937 | 0.78874 | 0.79687 | -0.00813 |
| 10 | 283.150 | 12.458 | 12.489 | -0.24 | 0.10296 | 0.78769 | 0.79361 | -0.00592 |
| 10 | 293.150 | 11.297 | 11.314 | -0.15 | 0.05654 | 0.78358 | 0.78721 | -0.00362 |
| 10 | 298.150 | 10.499 | 10.498 | 0.01  | 0.03333 | 0.78193 | 0.78175 | 0.00019  |
| 10 | 302.150 | 9.544  | 9.543  | 0.01  | 0.01476 | 0.77510 | 0.77487 | 0.00022  |
| 10 | 303.150 | 9.201  | 9.196  | 0.05  | 0.01012 | 0.77416 | 0.77239 | 0.00177  |
| 10 | 304.150 | 8.737  | 8.730  | 0.08  | 0.00548 | 0.77227 | 0.76922 | 0.00305  |
| 10 | 305.150 | 7.830  | 7.820  | 0.13  | 0.00084 | 0.77224 | 0.76411 | 0.00813  |

NP = 29, RMSPCT = 0.142



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Table 7. Ethane liquid data not used for least squares.

| ID | T, K    | MOL/L  | CALC   | PCNT  | X       | YX      | YC      | YDIF     |
|----|---------|--------|--------|-------|---------|---------|---------|----------|
| 9  | 100.000 | 21.371 | 21.316 | 0.26  | 0.95311 | 0.86067 | 0.73872 | 0.12196  |
| 9  | 120.000 | 20.549 | 20.593 | -0.21 | 0.86028 | 0.71692 | 0.75003 | -0.03311 |
| 9  | 140.000 | 19.777 | 19.859 | -0.41 | 0.76744 | 0.72238 | 0.76064 | -0.03826 |
| 9  | 160.000 | 19.050 | 19.105 | -0.29 | 0.67460 | 0.75146 | 0.77044 | -0.01898 |
| 9  | 180.000 | 18.337 | 18.320 | 0.10  | 0.58176 | 0.78411 | 0.77926 | 0.00484  |
| 9  | 200.000 | 17.595 | 17.485 | 0.63  | 0.48893 | 0.81258 | 0.78690 | 0.02567  |
| 9  | 220.000 | 16.755 | 16.577 | 1.07  | 0.39609 | 0.82969 | 0.79304 | 0.03665  |
| 9  | 240.000 | 15.782 | 15.557 | 1.45  | 0.30325 | 0.83996 | 0.79719 | 0.04277  |
| 9  | 260.000 | 14.638 | 14.351 | 2.00  | 0.21042 | 0.85097 | 0.79845 | 0.05252  |
| 9  | 280.000 | 13.183 | 12.792 | 3.05  | 0.11758 | 0.86915 | 0.79489 | 0.07426  |
| 9  | 290.000 | 12.122 | 11.729 | 3.35  | 0.07116 | 0.87113 | 0.78971 | 0.08143  |
| 9  | 300.000 | 10.516 | 10.112 | 4.00  | 0.02474 | 0.88848 | 0.77899 | 0.10949  |
| 10 | 305.250 | 7.600  | 7.583  | 0.22  | 0.00037 | 0.78096 | 0.76316 | 0.01780  |
| 11 | 283.200 | 12.423 | 12.484 | -0.49 | 0.10272 | 0.78179 | 0.79359 | -0.01180 |
| 11 | 288.190 | 11.895 | 11.946 | -0.43 | 0.07956 | 0.78051 | 0.79092 | -0.01041 |
| 11 | 293.180 | 11.270 | 11.309 | -0.34 | 0.05640 | 0.77867 | 0.78718 | -0.00851 |
| 11 | 295.670 | 10.899 | 10.934 | -0.32 | 0.04484 | 0.77672 | 0.78474 | -0.00802 |
| 11 | 298.170 | 10.472 | 10.494 | -0.21 | 0.03324 | 0.77610 | 0.78172 | -0.00562 |
| 11 | 300.660 | 9.937  | 9.955  | -0.18 | 0.02168 | 0.77281 | 0.77785 | -0.00504 |
| 11 | 302.160 | 9.534  | 9.540  | -0.07 | 0.01471 | 0.77282 | 0.77485 | -0.00203 |
| 11 | 303.160 | 9.190  | 9.192  | -0.02 | 0.01007 | 0.77159 | 0.77236 | -0.00078 |
| 11 | 304.150 | 8.732  | 8.730  | 0.02  | 0.00548 | 0.76994 | 0.76922 | 0.00072  |
| 11 | 304.650 | 8.397  | 8.395  | 0.03  | 0.00316 | 0.76825 | 0.76713 | 0.00112  |
| 11 | 305.150 | 7.827  | 7.820  | 0.09  | 0.00084 | 0.77012 | 0.76411 | 0.00601  |
| 13 | 105.372 | 21.105 | 21.122 | -0.08 | 0.92818 | 0.71576 | 0.74182 | -0.02606 |
| 13 | 99.817  | 21.298 | 21.323 | -0.11 | 0.95396 | 0.68284 | 0.73861 | -0.05577 |
| 13 | 94.261  | 21.490 | 21.523 | -0.15 | 0.97975 | 0.56468 | 0.73535 | -0.17068 |
| 16 | 283.200 | 12.434 | 12.484 | -0.39 | 0.10272 | 0.78404 | 0.79359 | -0.00955 |
| 16 | 288.190 | 11.909 | 11.946 | -0.31 | 0.07956 | 0.78335 | 0.79092 | -0.00757 |
| 16 | 293.180 | 11.290 | 11.309 | -0.17 | 0.05640 | 0.78302 | 0.78718 | -0.00416 |
| 16 | 295.670 | 10.924 | 10.934 | -0.08 | 0.04484 | 0.78262 | 0.78474 | -0.00211 |
| 16 | 298.170 | 10.502 | 10.494 | 0.07  | 0.03324 | 0.78367 | 0.78172 | 0.00195  |
| 16 | 300.660 | 9.980  | 9.955  | 0.25  | 0.02168 | 0.78497 | 0.77785 | 0.00712  |
| 16 | 302.160 | 9.578  | 9.540  | 0.39  | 0.01471 | 0.78669 | 0.77485 | 0.01184  |

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Table 8. Calculated oxygen liquid densities

| T, K    | R, MOL/L | DR/DT   | D2R/DT2  |
|---------|----------|---------|----------|
| 54.351  | 40.830   | -0.1377 | -0.00019 |
| 56.000  | 40.603   | -0.1380 | -0.00021 |
| 58.000  | 40.326   | -0.1385 | -0.00023 |
| 60.000  | 40.049   | -0.1390 | -0.00026 |
| 62.000  | 39.770   | -0.1395 | -0.00029 |
| 64.000  | 39.491   | -0.1401 | -0.00032 |
| 66.000  | 39.210   | -0.1408 | -0.00035 |
| 68.000  | 38.928   | -0.1415 | -0.00038 |
| 70.000  | 38.644   | -0.1423 | -0.00041 |
| 72.000  | 38.358   | -0.1432 | -0.00045 |
| 74.000  | 38.071   | -0.1441 | -0.00049 |
| 76.000  | 37.782   | -0.1451 | -0.00053 |
| 78.000  | 37.491   | -0.1462 | -0.00057 |
| 80.000  | 37.197   | -0.1474 | -0.00061 |
| 82.000  | 36.901   | -0.1487 | -0.00066 |
| 84.000  | 36.602   | -0.1500 | -0.00071 |
| 86.000  | 36.301   | -0.1515 | -0.00077 |
| 88.000  | 35.996   | -0.1531 | -0.00083 |
| 90.000  | 35.688   | -0.1548 | -0.00089 |
| 92.000  | 35.377   | -0.1567 | -0.00096 |
| 94.000  | 35.062   | -0.1586 | -0.00103 |
| 96.000  | 34.742   | -0.1608 | -0.00111 |
| 98.000  | 34.418   | -0.1631 | -0.00119 |
| 100.000 | 34.090   | -0.1655 | -0.00129 |
| 102.000 | 33.756   | -0.1682 | -0.00139 |
| 104.000 | 33.417   | -0.1711 | -0.00150 |
| 106.000 | 33.072   | -0.1742 | -0.00162 |
| 108.000 | 32.720   | -0.1776 | -0.00176 |
| 110.000 | 32.361   | -0.1813 | -0.00191 |
| 112.000 | 31.995   | -0.1852 | -0.00207 |
| 114.000 | 31.620   | -0.1896 | -0.00226 |
| 116.000 | 31.236   | -0.1943 | -0.00248 |
| 118.000 | 30.842   | -0.1995 | -0.00272 |
| 120.000 | 30.438   | -0.2052 | -0.00300 |
| 122.000 | 30.021   | -0.2115 | -0.00332 |
| 124.000 | 29.591   | -0.2185 | -0.00369 |
| 126.000 | 29.147   | -0.2263 | -0.00413 |
| 128.000 | 28.685   | -0.2351 | -0.00466 |
| 130.000 | 28.205   | -0.2450 | -0.00530 |
| 132.000 | 27.704   | -0.2564 | -0.00608 |
| 134.000 | 27.179   | -0.2695 | -0.00707 |
| 136.000 | 26.625   | -0.2848 | -0.00833 |
| 138.000 | 26.037   | -0.3031 | -0.01000 |
| 140.000 | 25.410   | -0.3253 | -0.01229 |
| 142.000 | 24.733   | -0.3529 | -0.01555 |
| 144.000 | 23.993   | -0.3886 | -0.02051 |
| 146.000 | 23.170   | -0.4370 | -0.02869 |
| 148.000 | 22.230   | -0.5079 | -0.04396 |
| 150.000 | 21.108   | -0.6253 | -0.07893 |
| 152.000 | 19.647   | -0.8749 | -0.20084 |
| 154.000 | 17.104   | -2.1732 | -2.34479 |
| 154.576 | 13.630   | 0.0000  | 0.00000  |

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Table 9. Calculated fluorine liquid densities.

| T, K    | R, MOL/L | DR/DT   | D2R/DT2  |
|---------|----------|---------|----------|
| 53.481  | 44.862   | -0.1573 | -0.00054 |
| 54.000  | 44.781   | -0.1576 | -0.00055 |
| 56.000  | 44.464   | -0.1587 | -0.00058 |
| 58.000  | 44.146   | -0.1599 | -0.00061 |
| 60.000  | 43.825   | -0.1612 | -0.00065 |
| 62.000  | 43.501   | -0.1625 | -0.00068 |
| 64.000  | 43.174   | -0.1639 | -0.00072 |
| 66.000  | 42.845   | -0.1654 | -0.00076 |
| 68.000  | 42.513   | -0.1670 | -0.00081 |
| 70.000  | 42.177   | -0.1686 | -0.00085 |
| 72.000  | 41.838   | -0.1704 | -0.00090 |
| 74.000  | 41.496   | -0.1722 | -0.00095 |
| 76.000  | 41.149   | -0.1742 | -0.00101 |
| 78.000  | 40.799   | -0.1763 | -0.00107 |
| 80.000  | 40.444   | -0.1785 | -0.00114 |
| 82.000  | 40.085   | -0.1808 | -0.00121 |
| 84.000  | 39.720   | -0.1833 | -0.00129 |
| 86.000  | 39.351   | -0.1860 | -0.00137 |
| 88.000  | 38.976   | -0.1888 | -0.00146 |
| 90.000  | 38.596   | -0.1918 | -0.00156 |
| 92.000  | 38.209   | -0.1951 | -0.00167 |
| 94.000  | 37.815   | -0.1985 | -0.00179 |
| 96.000  | 37.415   | -0.2022 | -0.00192 |
| 98.000  | 37.006   | -0.2062 | -0.00207 |
| 100.000 | 36.590   | -0.2105 | -0.00223 |
| 102.000 | 36.164   | -0.2151 | -0.00242 |
| 104.000 | 35.729   | -0.2202 | -0.00262 |
| 106.000 | 35.283   | -0.2257 | -0.00286 |
| 108.000 | 34.826   | -0.2316 | -0.00313 |
| 110.000 | 34.356   | -0.2382 | -0.00344 |
| 112.000 | 33.873   | -0.2454 | -0.00380 |
| 114.000 | 33.374   | -0.2534 | -0.00422 |
| 116.000 | 32.858   | -0.2624 | -0.00472 |
| 118.000 | 32.324   | -0.2724 | -0.00533 |
| 120.000 | 31.768   | -0.2838 | -0.00606 |
| 122.000 | 31.188   | -0.2967 | -0.00696 |
| 124.000 | 30.579   | -0.3118 | -0.00811 |
| 126.000 | 29.939   | -0.3294 | -0.00959 |
| 128.000 | 29.260   | -0.3505 | -0.01156 |
| 130.000 | 28.534   | -0.3762 | -0.01428 |
| 132.000 | 27.751   | -0.4084 | -0.01821 |
| 134.000 | 26.894   | -0.4504 | -0.02426 |
| 136.000 | 25.939   | -0.5081 | -0.03440 |
| 138.000 | 24.843   | -0.5939 | -0.05377 |
| 140.000 | 23.524   | -0.7400 | -0.09999 |
| 142.000 | 21.770   | -1.0696 | -0.27704 |
| 144.000 | 18.328   | -3.6894 | -7.49794 |
| 144.310 | 15.150   | 0.0000  | 0.00000  |



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Table 10. Calculated methane liquid densities

| T, K    | R, MOL/L | DR/DT   | D2R/DT2  |
|---------|----------|---------|----------|
| 90.680  | 28.147   | -0.0825 | -0.00031 |
| 92.000  | 28.038   | -0.0829 | -0.00032 |
| 94.000  | 27.871   | -0.0836 | -0.00033 |
| 96.000  | 27.704   | -0.0842 | -0.00035 |
| 98.000  | 27.534   | -0.0849 | -0.00036 |
| 100.000 | 27.364   | -0.0857 | -0.00038 |
| 102.000 | 27.192   | -0.0865 | -0.00040 |
| 104.000 | 27.018   | -0.0873 | -0.00041 |
| 106.000 | 26.843   | -0.0881 | -0.00043 |
| 108.000 | 26.665   | -0.0890 | -0.00045 |
| 110.000 | 26.486   | -0.0899 | -0.00048 |
| 112.000 | 26.306   | -0.0909 | -0.00050 |
| 114.000 | 26.123   | -0.0919 | -0.00052 |
| 116.000 | 25.938   | -0.0930 | -0.00055 |
| 118.000 | 25.751   | -0.0941 | -0.00058 |
| 120.000 | 25.561   | -0.0953 | -0.00061 |
| 122.000 | 25.369   | -0.0966 | -0.00064 |
| 124.000 | 25.175   | -0.0979 | -0.00068 |
| 126.000 | 24.978   | -0.0993 | -0.00072 |
| 128.000 | 24.778   | -0.1008 | -0.00076 |
| 130.000 | 24.575   | -0.1023 | -0.00080 |
| 132.000 | 24.368   | -0.1040 | -0.00085 |
| 134.000 | 24.158   | -0.1057 | -0.00090 |
| 136.000 | 23.945   | -0.1076 | -0.00096 |
| 138.000 | 23.728   | -0.1096 | -0.00103 |
| 140.000 | 23.507   | -0.1117 | -0.00110 |
| 142.000 | 23.281   | -0.1140 | -0.00117 |
| 144.000 | 23.051   | -0.1164 | -0.00126 |
| 146.000 | 22.815   | -0.1190 | -0.00136 |
| 148.000 | 22.574   | -0.1219 | -0.00147 |
| 150.000 | 22.328   | -0.1249 | -0.00159 |
| 152.000 | 22.075   | -0.1282 | -0.00173 |
| 154.000 | 21.815   | -0.1318 | -0.00188 |
| 156.000 | 21.547   | -0.1358 | -0.00207 |
| 158.000 | 21.271   | -0.1401 | -0.00228 |
| 160.000 | 20.986   | -0.1449 | -0.00253 |
| 162.000 | 20.691   | -0.1503 | -0.00282 |
| 164.000 | 20.385   | -0.1562 | -0.00318 |
| 166.000 | 20.066   | -0.1630 | -0.00361 |
| 168.000 | 19.732   | -0.1707 | -0.00414 |
| 170.000 | 19.382   | -0.1797 | -0.00481 |
| 172.000 | 19.012   | -0.1901 | -0.00568 |
| 174.000 | 18.620   | -0.2026 | -0.00683 |
| 176.000 | 18.200   | -0.2177 | -0.00841 |
| 178.000 | 17.747   | -0.2367 | -0.01068 |
| 180.000 | 17.250   | -0.2612 | -0.01415 |
| 182.000 | 16.696   | -0.2947 | -0.01988 |
| 184.000 | 16.061   | -0.3440 | -0.03064 |
| 186.000 | 15.299   | -0.4261 | -0.05538 |
| 188.000 | 14.298   | -0.6021 | -0.14217 |
| 190.000 | 12.527   | -1.5385 | -1.72796 |
| 190.555 | 10.200   | 0.0000  | 0.00000  |

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SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME

R.D. Goodwin

DATE

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Table 11. Calculated ethane liquid densities.

## ETHANE SATURATED LIQUID DENSITIES

| T, K    | R, MOL/L | DR/DT   | D2R/DT2  |
|---------|----------|---------|----------|
| 89.899  | 21.680   | -0.0360 | 0.00000  |
| 90.000  | 21.676   | -0.0360 | 0.00000  |
| 95.000  | 21.496   | -0.0360 | -0.00000 |
| 100.000 | 21.316   | -0.0360 | -0.00001 |
| 105.000 | 21.136   | -0.0361 | -0.00001 |
| 110.000 | 20.955   | -0.0362 | -0.00002 |
| 115.000 | 20.774   | -0.0363 | -0.00002 |
| 120.000 | 20.593   | -0.0364 | -0.00003 |
| 125.000 | 20.411   | -0.0365 | -0.00003 |
| 130.000 | 20.228   | -0.0367 | -0.00004 |
| 135.000 | 20.044   | -0.0369 | -0.00004 |
| 140.000 | 19.859   | -0.0371 | -0.00005 |
| 145.000 | 19.673   | -0.0374 | -0.00006 |
| 150.000 | 19.485   | -0.0377 | -0.00006 |
| 155.000 | 19.296   | -0.0380 | -0.00007 |
| 160.000 | 19.105   | -0.0384 | -0.00008 |
| 165.000 | 18.912   | -0.0388 | -0.00009 |
| 170.000 | 18.717   | -0.0392 | -0.00010 |
| 175.000 | 18.520   | -0.0398 | -0.00011 |
| 180.000 | 18.320   | -0.0403 | -0.00012 |
| 185.000 | 18.116   | -0.0410 | -0.00013 |
| 190.000 | 17.910   | -0.0417 | -0.00015 |
| 195.000 | 17.700   | -0.0424 | -0.00016 |
| 200.000 | 17.485   | -0.0433 | -0.00018 |
| 205.000 | 17.266   | -0.0443 | -0.00020 |
| 210.000 | 17.042   | -0.0453 | -0.00022 |
| 215.000 | 16.813   | -0.0465 | -0.00025 |
| 220.000 | 16.577   | -0.0478 | -0.00028 |
| 225.000 | 16.335   | -0.0493 | -0.00031 |
| 230.000 | 16.085   | -0.0509 | -0.00035 |
| 235.000 | 15.826   | -0.0527 | -0.00039 |
| 240.000 | 15.557   | -0.0548 | -0.00045 |
| 245.000 | 15.277   | -0.0572 | -0.00051 |
| 250.000 | 14.984   | -0.0600 | -0.00059 |
| 255.000 | 14.676   | -0.0632 | -0.00069 |
| 260.000 | 14.351   | -0.0669 | -0.00082 |
| 265.000 | 14.005   | -0.0715 | -0.00099 |
| 270.000 | 13.635   | -0.0770 | -0.00123 |
| 275.000 | 13.233   | -0.0839 | -0.00156 |
| 280.000 | 12.792   | -0.0929 | -0.00208 |
| 285.000 | 12.299   | -0.1053 | -0.00295 |
| 290.000 | 11.729   | -0.1238 | -0.00463 |
| 295.000 | 11.040   | -0.1554 | -0.00871 |
| 300.000 | 10.112   | -0.2288 | -0.02539 |
| 305.000 | 8.048    | -1.2696 | -2.44167 |
| 305.330 | 6.870    | 0.0000  | 0.00000  |



## LABORATORY NOTE

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NAME

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Table 12. Comparison of oxygen vapor densities.

$$E = 0.382$$

TCRT = 154.576, TTRP = 54.3507

DCRT = 13.630, DTRP = 3.36122-004

2.7737066-001 -3.3866205-001 7.6907075-001 -1.5761185+000  
9.3987130-001 0.0000000+000 0.0000000+000 0.0000000+000

| ID | T, K    | MOL/L      | CALCD      | PCNT  | Z        | YX      | YC      | YDIF     |
|----|---------|------------|------------|-------|----------|---------|---------|----------|
| 99 | 56.000  | 5.3300-004 | 5.3288-004 | 0.02  | 0.95458  | 0.07082 | 0.07159 | -0.00077 |
| 99 | 58.000  | 8.9930-004 | 8.9941-004 | -0.01 | 0.90296  | 0.07289 | 0.07270 | 0.00019  |
| 99 | 60.000  | 1.4640-003 | 1.4644-003 | -0.03 | 0.85479  | 0.07505 | 0.07474 | 0.00031  |
| 99 | 62.000  | 2.3057-003 | 2.3068-003 | -0.05 | 0.80972  | 0.07792 | 0.07752 | 0.00040  |
| 99 | 64.000  | 3.5233-003 | 3.5251-003 | -0.05 | 0.76747  | 0.08123 | 0.08089 | 0.00034  |
| 99 | 66.000  | 5.2367-003 | 5.2386-003 | -0.04 | 0.72778  | 0.08497 | 0.08473 | 0.00024  |
| 99 | 68.000  | 7.5880-003 | 7.5899-003 | -0.02 | 0.69042  | 0.08906 | 0.08893 | 0.00013  |
| 99 | 70.000  | 1.0742-002 | 1.0742-002 | -0.00 | 0.65520  | 0.09343 | 0.09341 | 0.00001  |
| 99 | 72.000  | 1.4685-002 | 1.4683-002 | 0.01  | 0.62194  | 0.09804 | 0.09811 | -0.00006 |
| 99 | 74.000  | 2.0227-002 | 2.0220-002 | 0.04  | 0.59048  | 0.10281 | 0.10296 | -0.00015 |
| 99 | 76.000  | 2.6996-002 | 2.6983-002 | 0.05  | 0.56067  | 0.10773 | 0.10792 | -0.00019 |
| 99 | 78.000  | 3.5441-002 | 3.5421-002 | 0.06  | 0.53239  | 0.11275 | 0.11296 | -0.00021 |
| 99 | 80.000  | 4.5831-002 | 4.5802-002 | 0.06  | 0.50552  | 0.11781 | 0.11804 | -0.00023 |
| 99 | 82.000  | 5.8449-002 | 5.8412-002 | 0.06  | 0.47996  | 0.12292 | 0.12314 | -0.00022 |
| 99 | 84.000  | 7.3595-002 | 7.3552-002 | 0.06  | 0.45562  | 0.12804 | 0.12823 | -0.00019 |
| 99 | 86.000  | 9.1589-002 | 9.1542-002 | 0.05  | 0.43242  | 0.13313 | 0.13330 | -0.00017 |
| 99 | 88.000  | 1.1276-001 | 1.1271-001 | 0.04  | 0.41026  | 0.13821 | 0.13833 | -0.00012 |
| 99 | 90.000  | 1.3745-001 | 1.3741-001 | 0.03  | 0.38910  | 0.14323 | 0.14331 | -0.00008 |
| 99 | 92.000  | 1.6603-001 | 1.6601-001 | 0.01  | 0.36885  | 0.14820 | 0.14824 | -0.00004 |
| 99 | 94.000  | 1.9887-001 | 1.9887-001 | -0.00 | 0.34946  | 0.15311 | 0.15310 | 0.00000  |
| 99 | 96.000  | 2.3637-001 | 2.3641-001 | -0.01 | 0.33088  | 0.15794 | 0.15790 | 0.00004  |
| 99 | 98.000  | 2.7894-001 | 2.7902-001 | -0.03 | 0.31306  | 0.16270 | 0.16262 | 0.00008  |
| 99 | 100.000 | 3.2702-001 | 3.2716-001 | -0.04 | 0.29596  | 0.16738 | 0.16726 | 0.00012  |
| 99 | 102.000 | 3.8108-001 | 3.8127-001 | -0.05 | 0.27952  | 0.17196 | 0.17182 | 0.00014  |
| 99 | 104.000 | 4.4162-001 | 4.4186-001 | -0.05 | 0.26372  | 0.17645 | 0.17630 | 0.00015  |
| 99 | 106.000 | 5.0914-001 | 5.0943-001 | -0.06 | 0.24851  | 0.18086 | 0.18070 | 0.00016  |
| 99 | 108.000 | 5.8421-001 | 5.8455-001 | -0.06 | 0.23387  | 0.18518 | 0.18502 | 0.00016  |
| 99 | 110.000 | 6.6747-001 | 6.6783-001 | -0.05 | 0.21975  | 0.18940 | 0.18925 | 0.00015  |
| 99 | 112.000 | 7.5953-001 | 7.5992-001 | -0.05 | 0.20615  | 0.19355 | 0.19341 | 0.00014  |
| 99 | 114.000 | 8.6121-001 | 8.6155-001 | -0.04 | 0.19302  | 0.19759 | 0.19748 | 0.00011  |
| 99 | 116.000 | 9.7325-001 | 9.7353-001 | -0.03 | 0.18034  | 0.20156 | 0.20148 | 0.00008  |
| 99 | 118.000 | 1.0965+000 | 1.0967+000 | -0.02 | 0.16803  | 0.20545 | 0.20540 | 0.00005  |
| 99 | 120.000 | 1.2321+000 | 1.2322+000 | -0.00 | 0.15625  | 0.20926 | 0.20925 | 0.00000  |
| 99 | 122.000 | 1.3812+000 | 1.3810+000 | 0.01  | 0.14480  | 0.21299 | 0.21303 | -0.00004 |
| 99 | 124.000 | 1.5450+000 | 1.5445+000 | 0.03  | 0.13372  | 0.21666 | 0.21674 | -0.00008 |
| 99 | 126.000 | 1.7250+000 | 1.7243+000 | 0.04  | 0.12299  | 0.22027 | 0.22039 | -0.00012 |
| 99 | 128.000 | 1.9230+000 | 1.9220+000 | 0.05  | 0.11259  | 0.22383 | 0.22398 | -0.00015 |
| 99 | 130.000 | 2.1411+000 | 2.1399+000 | 0.06  | 0.10252  | 0.22735 | 0.22751 | -0.00017 |
| 99 | 132.000 | 2.3619+000 | 2.3605+000 | 0.06  | 0.09275  | 0.23083 | 0.23100 | -0.00017 |
| 99 | 134.000 | 2.6483+000 | 2.6470+000 | 0.05  | 0.08327  | 0.23429 | 0.23444 | -0.00016 |
| 99 | 136.000 | 2.9444+000 | 2.9433+000 | 0.04  | 0.07407  | 0.23773 | 0.23786 | -0.00012 |
| 99 | 138.000 | 3.2750+000 | 3.2745+000 | 0.01  | 0.066514 | 0.24119 | 0.24124 | -0.00005 |
| 99 | 140.000 | 3.6468+000 | 3.6474+000 | -0.02 | 0.05646  | 0.24468 | 0.24462 | 0.00006  |
| 99 | 142.000 | 4.0692+000 | 4.0712+000 | -0.05 | 0.04803  | 0.24819 | 0.24801 | 0.00018  |
| 99 | 144.000 | 4.5552+000 | 4.5592+000 | -0.09 | 0.03983  | 0.25176 | 0.25143 | 0.00033  |
| 99 | 146.000 | 5.1261+000 | 5.1316+000 | -0.11 | 0.03185  | 0.25536 | 0.25493 | 0.00043  |
| 99 | 148.000 | 5.8177+000 | 5.8225+000 | -0.08 | 0.02410  | 0.25892 | 0.25857 | 0.00035  |
| 99 | 150.000 | 6.7056+000 | 6.6967+000 | 0.13  | 0.01654  | 0.26182 | 0.26247 | -0.00065 |
| 99 | 152.000 | 7.9239+000 | 7.9138+000 | 0.13  | 0.00919  | 0.26616 | 0.26692 | -0.00076 |
| 99 | 154.000 | 1.0225+001 | 1.0230+001 | -0.05 | 0.00263  | 0.27367 | 0.27313 | 0.00054  |

NP = 53, RMSPO = 0.052

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NAME

R.D. Goodwin

DATE

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Table 13. Comparison of fluorine vapor densities.

$$E = 0.362$$

$$\begin{aligned} \text{TCRT} &= 144.310, \text{ TTRP} = 53.4811 \\ \text{DCRT} &= 15.150, \text{ DTRP} = 5.67000-004 \end{aligned}$$

$$\begin{aligned} 2.5715721-001 &-2.2706443-001 & 6.0538644-001 &-1.3916332+000 \\ 7.9257188-001 & 0.0000000+000 & 0.0000000+000 & 0.0000000+000 \end{aligned}$$

| ID | T,K     | MOL/L      | CALCD      | PCNT  | Z       | YX      | YC      | YDIF     |
|----|---------|------------|------------|-------|---------|---------|---------|----------|
| 98 | 54.000  | 6.6000-004 | 6.6001-004 | -0.00 | 0.98473 | 0.03779 | 0.03768 | 0.00010  |
| 98 | 56.000  | 1.1500-003 | 1.1518-003 | -0.16 | 0.92853 | 0.04645 | 0.04297 | 0.00348  |
| 98 | 58.000  | 1.9300-003 | 1.9272-003 | 0.14  | 0.87621 | 0.04693 | 0.04877 | -0.00184 |
| 98 | 60.000  | 3.1100-003 | 3.1038-003 | 0.20  | 0.82738 | 0.05309 | 0.05493 | -0.00184 |
| 98 | 62.000  | 4.8400-003 | 4.8291-003 | 0.23  | 0.78169 | 0.05968 | 0.06135 | -0.00167 |
| 98 | 64.000  | 7.2900-003 | 7.2821-003 | 0.11  | 0.73887 | 0.06725 | 0.06792 | -0.00067 |
| 98 | 66.000  | 1.0680-002 | 1.0675-002 | 0.05  | 0.69863 | 0.07434 | 0.07459 | -0.00026 |
| 98 | 68.000  | 1.5250-002 | 1.5253-002 | -0.02 | 0.66077 | 0.08139 | 0.08130 | 0.00009  |
| 98 | 70.000  | 2.1280-002 | 2.1293-002 | -0.06 | 0.62507 | 0.08827 | 0.08799 | 0.00028  |
| 98 | 72.000  | 2.9070-002 | 2.9105-002 | -0.12 | 0.59135 | 0.09515 | 0.09464 | 0.00051  |
| 98 | 74.000  | 3.8970-002 | 3.9029-002 | -0.15 | 0.55945 | 0.10181 | 0.10121 | 0.00060  |
| 98 | 76.000  | 5.1350-002 | 5.1434-002 | -0.16 | 0.52923 | 0.10829 | 0.10769 | 0.00060  |
| 98 | 78.000  | 6.6600-002 | 6.6713-002 | -0.17 | 0.50057 | 0.11466 | 0.11406 | 0.00060  |
| 98 | 80.000  | 8.5150-002 | 8.5291-002 | -0.17 | 0.47333 | 0.12086 | 0.12030 | 0.00056  |
| 98 | 82.000  | 1.0745-001 | 1.0761-001 | -0.15 | 0.44742 | 0.12691 | 0.12641 | 0.00050  |
| 98 | 84.000  | 1.3397-001 | 1.3416-001 | -0.14 | 0.42275 | 0.13281 | 0.13238 | 0.00044  |
| 98 | 86.000  | 1.6523-001 | 1.6541-001 | -0.11 | 0.39923 | 0.13854 | 0.13820 | 0.00034  |
| 98 | 88.000  | 2.0174-001 | 2.0191-001 | -0.08 | 0.37677 | 0.14413 | 0.14388 | 0.00025  |
| 98 | 90.000  | 2.4407-001 | 2.4420-001 | -0.05 | 0.35532 | 0.14956 | 0.14940 | 0.00015  |
| 98 | 92.000  | 2.9280-001 | 2.9286-001 | -0.02 | 0.33479 | 0.15484 | 0.15478 | 0.00006  |
| 98 | 94.000  | 3.4857-001 | 3.4852-001 | 0.01  | 0.31514 | 0.15997 | 0.16001 | -0.00004 |
| 98 | 96.000  | 4.1203-001 | 4.1184-001 | 0.05  | 0.29631 | 0.16496 | 0.16509 | -0.00013 |
| 98 | 98.000  | 4.8389-001 | 4.8352-001 | 0.08  | 0.27824 | 0.16981 | 0.17003 | -0.00021 |
| 98 | 100.000 | 5.6491-001 | 5.6432-001 | 0.10  | 0.26090 | 0.17453 | 0.17482 | -0.00029 |
| 98 | 102.000 | 6.5591-001 | 6.5507-001 | 0.13  | 0.24424 | 0.17912 | 0.17947 | -0.00035 |
| 98 | 104.000 | 7.5778-001 | 7.5667-001 | 0.15  | 0.22822 | 0.18358 | 0.18398 | -0.00040 |
| 98 | 106.000 | 8.7151-001 | 8.7012-001 | 0.16  | 0.21281 | 0.18792 | 0.18836 | -0.00044 |
| 98 | 108.000 | 9.9817-001 | 9.9651-001 | 0.17  | 0.19796 | 0.19215 | 0.19261 | -0.00046 |
| 98 | 110.000 | 1.1390+000 | 1.1371+000 | 0.17  | 0.18366 | 0.19627 | 0.19673 | -0.00046 |
| 98 | 112.000 | 1.2953+000 | 1.2932+000 | 0.16  | 0.16986 | 0.20028 | 0.20072 | -0.00044 |
| 98 | 114.000 | 1.4687+000 | 1.4666+000 | 0.15  | 0.15655 | 0.20419 | 0.20460 | -0.00041 |
| 98 | 116.000 | 1.6610+000 | 1.6590+000 | 0.12  | 0.14370 | 0.20801 | 0.20836 | -0.00035 |
| 98 | 118.000 | 1.8743+000 | 1.8725+000 | 0.09  | 0.13129 | 0.21174 | 0.21200 | -0.00027 |
| 98 | 120.000 | 2.1111+000 | 2.1099+000 | 0.06  | 0.11928 | 0.21538 | 0.21554 | -0.00016 |
| 98 | 122.000 | 2.3744+000 | 2.3741+000 | 0.01  | 0.10768 | 0.21894 | 0.21898 | -0.00004 |
| 98 | 124.000 | 2.6680+000 | 2.6690+000 | -0.04 | 0.09644 | 0.22243 | 0.22232 | 0.00011  |
| 98 | 126.000 | 2.9965+000 | 2.9992+000 | -0.09 | 0.08556 | 0.22584 | 0.22556 | 0.00027  |
| 98 | 128.000 | 3.3661+000 | 3.3709+000 | -0.14 | 0.07503 | 0.22917 | 0.22873 | 0.00045  |
| 98 | 130.000 | 3.7648+000 | 3.7921+000 | -0.19 | 0.06481 | 0.23243 | 0.23181 | 0.00062  |
| 98 | 132.000 | 4.2641+000 | 4.2739+000 | -0.23 | 0.05491 | 0.23560 | 0.23484 | 0.00076  |
| 98 | 134.000 | 4.8207+000 | 4.8319+000 | -0.23 | 0.04530 | 0.23862 | 0.23782 | 0.00081  |
| 98 | 136.000 | 5.4816+000 | 5.4905+000 | -0.16 | 0.03598 | 0.24138 | 0.24077 | 0.00061  |
| 98 | 138.000 | 6.2910+000 | 6.2909+000 | 0.00  | 0.02692 | 0.24374 | 0.24375 | -0.00001 |
| 98 | 140.000 | 7.3226+000 | 7.3133+000 | 0.13  | 0.01813 | 0.24625 | 0.24683 | -0.00058 |
| 98 | 142.000 | 8.7854+000 | 8.7644+000 | 0.24  | 0.00958 | 0.24889 | 0.25023 | -0.00133 |
| 98 | 144.000 | 1.1888+001 | 1.1893+001 | -0.04 | 0.00127 | 0.25552 | 0.25509 | 0.00044  |

$$\text{NP} = 46, \text{ RMSPCT} = 0.134$$

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NAME

R.D. Goodwin

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Table 14. Comparison of methane vapor densities.

$$E = 0.382$$

$$TCRT = 190.555, TTRP = 90.6800$$

$$DCRT = 10.200, DTRP = 1.56787-002$$

$$3.7413143-001 \quad -2.6157309-001 \quad 6.7533217-001 \quad -1.0122063+000$$

$$4.3988336-001 \quad 0.0000000+000 \quad 0.0000000+000 \quad 0.0000000+000$$

| ID   | T,K     | MOL/L      | CALCD      | PCNT  | Z       | YX      | YC      | YDIF     |
|------|---------|------------|------------|-------|---------|---------|---------|----------|
| 2    | 92.000  | 1.8280-002 | 1.8280-002 | 0.00  | 0.97263 | 0.21853 | 0.21874 | -0.00021 |
| 2    | 94.000  | 2.2860-002 | 2.2858-002 | 0.01  | 0.93261 | 0.22329 | 0.22354 | -0.00025 |
| 2    | 96.000  | 2.8290-002 | 2.8294-002 | -0.01 | 0.89427 | 0.22864 | 0.22828 | 0.00036  |
| 2    | 98.000  | 3.4690-002 | 3.4691-002 | -0.00 | 0.85749 | 0.23301 | 0.23295 | 0.00006  |
| 2    | 100.000 | 4.2160-002 | 4.2159-002 | 0.00  | 0.82218 | 0.23752 | 0.23755 | -0.00003 |
| 2    | 102.000 | 5.0810-002 | 5.0813-002 | -0.01 | 0.78826 | 0.24213 | 0.24207 | 0.00007  |
| 2    | 104.000 | 6.0770-002 | 6.0772-002 | -0.00 | 0.75564 | 0.24653 | 0.24650 | 0.00003  |
| 2    | 106.000 | 7.2160-002 | 7.2161-002 | -0.00 | 0.72425 | 0.25086 | 0.25084 | 0.00002  |
| 2    | 108.000 | 8.5110-002 | 8.5110-002 | -0.00 | 0.69402 | 0.25510 | 0.25510 | 0.00000  |
| 2    | 110.000 | 9.9750-002 | 9.9753-002 | -0.00 | 0.66490 | 0.25928 | 0.25926 | 0.00002  |
| 2    | 112.000 | 1.1623-001 | 1.1623-001 | 0.00  | 0.63681 | 0.26332 | 0.26333 | -0.00000 |
| 2    | 114.000 | 1.3468-001 | 1.3468-001 | -0.00 | 0.60971 | 0.26732 | 0.26730 | 0.00002  |
| 2    | 116.000 | 1.5527-001 | 1.5527-001 | 0.00  | 0.58354 | 0.27117 | 0.27119 | -0.00002 |
| 2    | 118.000 | 1.7814-001 | 1.7813-001 | 0.00  | 0.55826 | 0.27495 | 0.27498 | -0.00002 |
| 2    | 120.000 | 2.0346-001 | 2.0345-001 | 0.01  | 0.53383 | 0.27864 | 0.27868 | -0.00004 |
| 2    | 122.000 | 2.3139-001 | 2.3138-001 | 0.00  | 0.51019 | 0.28226 | 0.28228 | -0.00003 |
| 2    | 124.000 | 2.6212-001 | 2.6211-001 | 0.00  | 0.48732 | 0.28577 | 0.28580 | -0.00003 |
| 2    | 126.000 | 2.9583-001 | 2.9582-001 | 0.00  | 0.46517 | 0.28921 | 0.28923 | -0.00002 |
| 2    | 128.000 | 3.3272-001 | 3.3271-001 | 0.00  | 0.44372 | 0.29255 | 0.29257 | -0.00002 |
| 2    | 130.000 | 3.7299-001 | 3.7299-001 | 0.00  | 0.42292 | 0.29582 | 0.29583 | -0.00001 |
| 2    | 132.000 | 4.1686-001 | 4.1687-001 | -0.00 | 0.40276 | 0.29902 | 0.29900 | 0.00002  |
| 2    | 134.000 | 4.6457-001 | 4.6461-001 | -0.01 | 0.38320 | 0.30213 | 0.30209 | 0.00004  |
| 2    | 136.000 | 5.1638-001 | 5.1644-001 | -0.01 | 0.36421 | 0.30515 | 0.30510 | 0.00006  |
| 2    | 138.000 | 5.7255-001 | 5.7264-001 | -0.02 | 0.34577 | 0.30811 | 0.30803 | 0.00008  |
| 2    | 140.000 | 6.3337-001 | 6.3351-001 | -0.02 | 0.32786 | 0.31099 | 0.31088 | 0.00011  |
| 2    | 142.000 | 6.9916-001 | 6.9937-001 | -0.03 | 0.31046 | 0.31380 | 0.31366 | 0.00014  |
| 2    | 144.000 | 7.7028-001 | 7.7055-001 | -0.04 | 0.29353 | 0.31654 | 0.31637 | 0.00016  |
| 2    | 146.000 | 8.4711-001 | 8.4745-001 | -0.04 | 0.27708 | 0.31920 | 0.31901 | 0.00019  |
| 2    | 148.000 | 9.3007-001 | 9.3049-001 | -0.05 | 0.26106 | 0.32179 | 0.32158 | 0.00021  |
| 2    | 150.000 | 1.0196+000 | 1.0201+000 | -0.05 | 0.24548 | 0.32431 | 0.32409 | 0.00022  |
| 2    | 152.000 | 1.1164+000 | 1.1169+000 | -0.05 | 0.23030 | 0.32675 | 0.32653 | 0.00022  |
| 2    | 154.000 | 1.2209+000 | 1.2214+000 | -0.05 | 0.21552 | 0.32912 | 0.32891 | 0.00021  |
| 2    | 156.000 | 1.3338+000 | 1.3343+000 | -0.04 | 0.20111 | 0.33140 | 0.33123 | 0.00017  |
| 2    | 158.000 | 1.4560+000 | 1.4563+000 | -0.02 | 0.18707 | 0.33361 | 0.33350 | 0.00011  |
| 2    | 160.000 | 1.5884+000 | 1.5884+000 | -0.00 | 0.17339 | 0.33571 | 0.33571 | 0.00000  |
| 2    | 162.000 | 1.7322+000 | 1.7316+000 | 0.03  | 0.16004 | 0.33772 | 0.33788 | -0.00016 |
| 2    | 164.000 | 1.8886+000 | 1.8870+000 | 0.08  | 0.14701 | 0.33951 | 0.34000 | -0.00039 |
| 2    | 166.000 | 2.0593+000 | 2.0561+000 | 0.16  | 0.13430 | 0.34135 | 0.34208 | -0.00073 |
| 2    | 168.000 | 2.2465+000 | 2.2406+000 | 0.26  | 0.12190 | 0.34291 | 0.34412 | -0.00121 |
| 1610 | 163.167 | 2.3488+000 | 2.3463+000 | 0.11  | 0.11540 | 0.34469 | 0.34520 | -0.00051 |
| 1614 | 163.270 | 2.3687+000 | 2.3670+000 | 0.07  | 0.11417 | 0.34506 | 0.34540 | -0.00035 |
| 912  | 163.417 | 2.3858+000 | 2.3821+000 | 0.16  | 0.11328 | 0.34480 | 0.34555 | -0.00075 |
| 1612 | 163.468 | 2.3981+000 | 2.3873+000 | 0.03  | 0.11297 | 0.34545 | 0.34560 | -0.00015 |
| 910  | 163.601 | 2.4054+000 | 2.4011+000 | 0.18  | 0.11217 | 0.34488 | 0.34573 | -0.00085 |
| 308  | 163.794 | 2.4036+000 | 2.4213+000 | 0.10  | 0.11101 | 0.34547 | 0.34593 | -0.00046 |
| 1716 | 173.088 | 2.7472+000 | 2.7964+000 | 0.03  | 0.09162 | 0.34905 | 0.34920 | -0.00015 |
| 1714 | 173.290 | 2.8263+000 | 2.8215+000 | -0.04 | 0.09046 | 0.34961 | 0.34940 | 0.00021  |



## LABORATORY NOTE

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## SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

## NAME

R.D. Goodwin

## DATE

Sept. 18, 1973

Table 14 (Continued). Methane vapor densities.

| ID                      | T, K    | MOL/L      | CALCD      | PCNT  | Z       | YX      | YC      | YDIF     |
|-------------------------|---------|------------|------------|-------|---------|---------|---------|----------|
| 1712                    | 173.489 | 2.8457+000 | 2.8465+000 | -0.03 | 0.08931 | 0.34973 | 0.34959 | 0.00014  |
| 1012                    | 173.473 | 2.8480+000 | 2.8445+000 | 0.12  | 0.08940 | 0.34896 | 0.34958 | -0.00062 |
| 1010                    | 173.675 | 2.8700+000 | 2.8701+000 | -0.00 | 0.08824 | 0.34980 | 0.34978 | 0.00002  |
| 1008                    | 173.857 | 2.8935+000 | 2.8934+000 | 0.00  | 0.08720 | 0.34995 | 0.34996 | -0.00001 |
| 1816                    | 177.094 | 3.3501+000 | 3.3513+000 | -0.03 | 0.06901 | 0.35333 | 0.35315 | 0.00018  |
| 1814                    | 177.292 | 3.3801+000 | 3.3822+000 | -0.06 | 0.06792 | 0.35369 | 0.35335 | 0.00034  |
| 1114                    | 177.328 | 3.3863+000 | 3.3879+000 | -0.05 | 0.06772 | 0.35364 | 0.35339 | 0.00025  |
| 1812                    | 177.485 | 3.4108+000 | 3.4128+000 | -0.06 | 0.06686 | 0.35386 | 0.35354 | 0.00031  |
| 1112                    | 177.509 | 3.4209+000 | 3.4166+000 | 0.12  | 0.06673 | 0.35290 | 0.35357 | -0.00067 |
| 1110                    | 177.700 | 3.4602+000 | 3.4473+000 | 0.37  | 0.06568 | 0.35175 | 0.35376 | -0.00200 |
| 1916                    | 181.105 | 4.0663+000 | 4.0686+000 | -0.06 | 0.04738 | 0.35755 | 0.35722 | 0.00033  |
| 1914                    | 181.304 | 4.1077+000 | 4.1101+000 | -0.06 | 0.04633 | 0.35778 | 0.35743 | 0.00034  |
| 1213                    | 181.389 | 4.1269+000 | 4.1281+000 | -0.03 | 0.04588 | 0.35769 | 0.35752 | 0.00017  |
| 1912                    | 181.506 | 4.1496+000 | 4.1530+000 | -0.08 | 0.04527 | 0.35813 | 0.35765 | 0.00048  |
| 1211                    | 181.589 | 4.1656+000 | 4.1708+000 | -0.12 | 0.04483 | 0.35848 | 0.35774 | 0.00074  |
| 1209                    | 181.768 | 4.2042+000 | 4.2097+000 | -0.13 | 0.04389 | 0.35870 | 0.35793 | 0.00078  |
| 1516                    | 183.117 | 4.5212+000 | 4.5240+000 | -0.06 | 0.03688 | 0.35978 | 0.35940 | 0.00038  |
| 1514                    | 183.322 | 4.5704+000 | 4.5754+000 | -0.11 | 0.03582 | 0.36032 | 0.35963 | 0.00069  |
| 1512                    | 183.514 | 4.6189+000 | 4.6246+000 | -0.12 | 0.03484 | 0.36063 | 0.35985 | 0.00078  |
| 1316                    | 184.125 | 4.7822+000 | 4.7880+000 | -0.12 | 0.03171 | 0.36134 | 0.36055 | 0.00079  |
| 2108                    | 184.387 | 4.7825+000 | 4.7775+000 | 0.10  | 0.03190 | 0.35982 | 0.36051 | -0.00068 |
| 2107                    | 184.285 | 4.8263+000 | 4.8327+000 | -0.13 | 0.03089 | 0.36161 | 0.36074 | 0.00087  |
| 1314                    | 184.370 | 4.8462+000 | 4.8567+000 | -0.22 | 0.03046 | 0.36228 | 0.36084 | 0.00144  |
| 2106                    | 184.471 | 4.8797+000 | 4.8857+000 | -0.12 | 0.02994 | 0.36177 | 0.36096 | 0.00081  |
| 1312                    | 184.510 | 4.8876+000 | 4.8969+000 | -0.19 | 0.02975 | 0.36228 | 0.36101 | 0.00127  |
| 6                       | 185.030 | 5.0380+000 | 5.0524+000 | -0.28 | 0.02711 | 0.36359 | 0.36164 | 0.00195  |
| 6                       | 185.030 | 5.3840+000 | 5.3838+000 | 0.00  | 0.02208 | 0.36290 | 0.36292 | -0.00002 |
| 2208                    | 186.103 | 5.4077+000 | 5.4098+000 | -0.04 | 0.02172 | 0.36331 | 0.36302 | 0.00029  |
| 1416                    | 186.129 | 5.4096+000 | 5.4192+000 | -0.18 | 0.02159 | 0.36436 | 0.36305 | 0.00131  |
| 1414                    | 186.319 | 5.4795+000 | 5.4891+000 | -0.17 | 0.02064 | 0.36461 | 0.36331 | 0.00130  |
| 2207                    | 186.304 | 5.4827+000 | 5.4835+000 | -0.01 | 0.02072 | 0.36339 | 0.36329 | 0.00010  |
| 2206                    | 186.501 | 5.5571+000 | 5.5581+000 | -0.02 | 0.01974 | 0.36369 | 0.36356 | 0.00013  |
| 1412                    | 186.518 | 5.5591+000 | 5.5646+000 | -0.10 | 0.01965 | 0.36434 | 0.36359 | 0.00075  |
| 6                       | 187.031 | 5.7860+000 | 5.7723+000 | 0.24  | 0.01711 | 0.36244 | 0.36433 | -0.00189 |
| 6                       | 188.031 | 6.2750+000 | 6.2474+000 | 0.44  | 0.01219 | 0.36201 | 0.36592 | -0.00392 |
| 2308                    | 188.140 | 6.2930+000 | 6.3064+000 | -0.21 | 0.01165 | 0.36804 | 0.36612 | 0.00193  |
| 2307                    | 188.343 | 6.4067+000 | 6.4218+000 | -0.24 | 0.01066 | 0.36868 | 0.36648 | 0.00219  |
| 2306                    | 188.545 | 6.5278+000 | 6.5441+000 | -0.25 | 0.00968 | 0.36926 | 0.36686 | 0.00239  |
| 6                       | 189.032 | 6.9180+000 | 6.8777+000 | 0.59  | 0.00732 | 0.36167 | 0.36787 | -0.00620 |
| 5                       | 189.765 | 7.5510+000 | 7.5576+000 | -0.09 | 0.00378 | 0.37093 | 0.36975 | 0.00117  |
| 6                       | 190.032 | 7.9600+000 | 7.9153+000 | 0.56  | 0.00250 | 0.36186 | 0.37065 | -0.00879 |
| 5                       | 190.046 | 7.9350+000 | 7.9371+000 | -0.03 | 0.00243 | 0.37113 | 0.37070 | 0.00043  |
| 7                       | 190.070 | 8.0000+000 | 7.9756+000 | 0.31  | 0.00232 | 0.36588 | 0.37079 | -0.00491 |
| 7                       | 190.170 | 8.1700+000 | 8.1508+000 | 0.24  | 0.00184 | 0.36709 | 0.37120 | -0.00412 |
| 7                       | 190.270 | 8.3600+000 | 8.3595+000 | 0.01  | 0.00136 | 0.37154 | 0.37166 | -0.00013 |
| 5                       | 190.279 | 8.3920+000 | 8.3805+000 | 0.14  | 0.00132 | 0.36899 | 0.37171 | -0.00272 |
| 7                       | 190.370 | 8.6200+000 | 8.6242+000 | -0.05 | 0.00088 | 0.37333 | 0.37221 | 0.00112  |
| 7                       | 190.470 | 9.0000+000 | 9.0116+000 | -0.13 | 0.00041 | 0.37689 | 0.37291 | 0.00397  |
| 5                       | 190.500 | 9.1610+000 | 9.1867+000 | -0.28 | 0.00026 | 0.38333 | 0.37319 | 0.01014  |
| NP = 96, RMSPCT = 0.148 |         |            |            |       |         |         |         |          |

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D. Goodwin  
DATE Sept. 18, 1973

Table 15. Comparison of ethane vapor densities.

ETHANE SATURATED VAPOR DENSITIES, E = 0.362

TCRT = 305.330, TTRP = 89.8990

DCRT = 6.870, DIRP = 1.35114-006

| ID | T, K    | MOL/L      | CALCD      | PCNT  | Z       | YX       | YC       | YDIF     |
|----|---------|------------|------------|-------|---------|----------|----------|----------|
| 1  | 90.000  | 1.3863-006 | 1.3863-006 | 0.00  | 0.99841 | -0.07301 | -0.07257 | -0.00044 |
| 1  | 100.000 | 1.3347-005 | 1.3356-005 | -0.07 | 0.85684 | -0.05815 | -0.05863 | 0.00048  |
| 1  | 110.000 | 8.1612-005 | 8.1696-005 | -0.10 | 0.74101 | -0.04219 | -0.04262 | 0.00043  |
| 1  | 120.000 | 3.5552-004 | 3.5568-004 | -0.04 | 0.64448 | -0.02573 | -0.02587 | 0.00014  |
| 1  | 130.000 | 1.1970-003 | 1.1963-003 | 0.05  | 0.56281 | -0.00924 | -0.00911 | -0.00014 |
| 1  | 140.000 | 3.3033-003 | 3.2990-003 | 0.13  | 0.49280 | 0.00698  | 0.00728  | -0.00030 |
| 1  | 150.000 | 7.8043-003 | 7.7918-003 | 0.16  | 0.43213 | 0.02275  | 0.02309  | -0.00034 |
| 1  | 160.000 | 1.6308-002 | 1.6284-002 | 0.15  | 0.37904 | 0.03793  | 0.03823  | -0.00029 |
| 1  | 170.000 | 3.0899-002 | 3.0869-002 | 0.10  | 0.33219 | 0.05247  | 0.05266  | -0.00019 |
| 1  | 180.000 | 5.4111-002 | 5.4094-002 | 0.03  | 0.29056 | 0.06634  | 0.06639  | -0.00006 |
| 1  | 190.000 | 8.8911-002 | 8.8944-002 | -0.04 | 0.25330 | 0.07952  | 0.07945  | 0.00007  |
| 1  | 200.000 | 1.3872-001 | 1.3885-001 | -0.09 | 0.21977 | 0.09203  | 0.09186  | 0.00017  |
| 1  | 210.000 | 2.0750-001 | 2.0777-001 | -0.13 | 0.18943 | 0.10390  | 0.10367  | 0.00024  |
| 1  | 220.000 | 2.9992-001 | 3.0036-001 | -0.14 | 0.16185 | 0.11517  | 0.11491  | 0.00026  |
| 1  | 230.000 | 4.2172-001 | 4.2230-001 | -0.14 | 0.13667 | 0.12588  | 0.12563  | 0.00025  |
| 1  | 240.000 | 5.8025-001 | 5.8088-001 | -0.11 | 0.11359 | 0.13607  | 0.13586  | 0.00021  |
| 1  | 245.000 | 6.7626-001 | 6.7685-001 | -0.09 | 0.10276 | 0.14098  | 0.14081  | 0.00017  |
| 1  | 250.000 | 7.8551-001 | 7.8599-001 | -0.06 | 0.09236 | 0.14578  | 0.14566  | 0.00012  |
| 10 | 253.150 | 8.6310-001 | 8.6237-001 | 0.08  | 0.08601 | 0.14848  | 0.14865  | -0.00017 |
| 10 | 263.150 | 1.1530+000 | 1.1519+000 | 0.10  | 0.06689 | 0.15771  | 0.15791  | -0.00020 |
| 10 | 273.150 | 1.5370+000 | 1.5359+000 | 0.07  | 0.04916 | 0.16665  | 0.16681  | -0.00017 |
| 10 | 283.150 | 2.0670+000 | 2.0666+000 | 0.02  | 0.03269 | 0.17533  | 0.17538  | -0.00005 |
| 10 | 293.150 | 2.8800+000 | 2.8727+000 | 0.25  | 0.01734 | 0.18285  | 0.18362  | -0.00077 |
| 10 | 298.150 | 3.5020+000 | 3.5014+000 | 0.02  | 0.01005 | 0.18755  | 0.18761  | -0.00006 |
| 10 | 302.150 | 4.3070+000 | 4.3040+000 | 0.07  | 0.00439 | 0.19036  | 0.19069  | -0.00033 |
| 10 | 303.150 | 4.6040+000 | 4.6123+000 | -0.18 | 0.00300 | 0.19241  | 0.19143  | 0.00098  |
| 10 | 304.150 | 5.0350+000 | 5.0389+000 | -0.08 | 0.00162 | 0.19267  | 0.19214  | 0.00053  |
| 10 | 305.150 | 5.9130+000 | 5.9127+000 | 0.01  | 0.00025 | 0.19268  | 0.19275  | -0.00007 |
| 10 | 305.250 | 6.1500+000 | 6.1484+000 | 0.03  | 0.00011 | 0.19233  | 0.19278  | -0.00046 |

NP = 29, RMSPCT = 0.104



## LABORATORY NOTE

PROJECT NO.

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FILE NO.

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SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME

R.D. Goodwin

DATE

Sept 18, 1973

Table 16. Ethane vapor data not used for least squares.

| ID | T, K    | MOL/L      | CALCD      | PCNT  | Z       | YX      | YC      | YDIF     |
|----|---------|------------|------------|-------|---------|---------|---------|----------|
| 1  | 255.000 | 9.0997-001 | 9.1025-001 | -0.03 | 0.08236 | 0.15046 | 0.15040 | 0.00006  |
| 1  | 260.000 | 1.0522+000 | 1.0521+000 | 0.01  | 0.07275 | 0.15502 | 0.15504 | -0.00002 |
| 1  | 265.000 | 1.2154+000 | 1.2147+000 | 0.06  | 0.06351 | 0.15946 | 0.15959 | -0.00012 |
| 1  | 270.000 | 1.4041+000 | 1.4023+000 | 0.13  | 0.05460 | 0.16377 | 0.16405 | -0.00028 |
| 1  | 275.000 | 1.6245+000 | 1.6207+000 | 0.23  | 0.04602 | 0.16789 | 0.16842 | -0.00053 |
| 1  | 280.000 | 1.8861+000 | 1.8784+000 | 0.41  | 0.03775 | 0.17173 | 0.17271 | -0.00098 |
| 1  | 285.000 | 2.2047+000 | 2.1886+000 | 0.73  | 0.02977 | 0.17504 | 0.17693 | -0.00189 |
| 1  | 290.000 | 2.6107+000 | 2.5736+000 | 1.44  | 0.02206 | 0.17701 | 0.18106 | -0.00405 |
| 6  | 184.500 | 6.8910-002 | 6.8143-002 | 1.12  | 0.27329 | 0.07029 | 0.07235 | -0.00206 |
| 6  | 226.207 | 3.7705-001 | 3.7217-001 | 1.31  | 0.14596 | 0.11923 | 0.12162 | -0.00239 |
| 6  | 234.603 | 4.9353-001 | 4.9022-001 | 0.67  | 0.12581 | 0.12914 | 0.13040 | -0.00126 |
| 6  | 238.921 | 5.6437-001 | 5.6173-001 | 0.47  | 0.11599 | 0.13390 | 0.13478 | -0.00089 |
| 6  | 243.238 | 6.4280-001 | 6.4162-001 | 0.18  | 0.10652 | 0.13873 | 0.13908 | -0.00035 |
| 6  | 248.665 | 7.5717-001 | 7.5546-001 | 0.23  | 0.09509 | 0.14393 | 0.14437 | -0.00044 |
| 6  | 253.042 | 8.6348-001 | 8.5964-001 | 0.45  | 0.08623 | 0.14767 | 0.14855 | -0.00089 |
| 6  | 258.809 | 1.0219+000 | 1.0166+000 | 0.52  | 0.07501 | 0.15288 | 0.15394 | -0.00107 |
| 6  | 263.286 | 1.1611+000 | 1.1564+000 | 0.41  | 0.06664 | 0.15718 | 0.15804 | -0.00086 |
| 6  | 268.732 | 1.3571+000 | 1.3521+000 | 0.37  | 0.05683 | 0.16211 | 0.16292 | -0.00081 |
| 6  | 273.090 | 1.5403+000 | 1.5332+000 | 0.46  | 0.04926 | 0.16572 | 0.16676 | -0.00104 |
| 6  | 278.638 | 1.8108+000 | 1.8037+000 | 0.39  | 0.03997 | 0.17061 | 0.17155 | -0.00094 |
| 6  | 283.576 | 2.0862+000 | 2.0939+000 | -0.36 | 0.03201 | 0.17666 | 0.17574 | 0.00092  |
| 6  | 288.254 | 2.4115+000 | 2.4286+000 | -0.70 | 0.02472 | 0.18155 | 0.17963 | 0.00193  |
| 11 | 283.200 | 2.0685+000 | 2.0698+000 | -0.06 | 0.03261 | 0.17558 | 0.17542 | 0.00016  |
| 11 | 288.190 | 2.4160+000 | 2.4235+000 | -0.31 | 0.02482 | 0.18042 | 0.17957 | 0.00085  |
| 11 | 293.180 | 2.8716+000 | 2.8758+000 | -0.15 | 0.01729 | 0.18409 | 0.18365 | 0.00045  |
| 11 | 295.670 | 3.1543+000 | 3.1589+000 | -0.14 | 0.01363 | 0.18612 | 0.18565 | 0.00048  |
| 11 | 298.170 | 3.5002+000 | 3.5045+000 | -0.12 | 0.01002 | 0.18807 | 0.18763 | 0.00044  |
| 11 | 300.660 | 3.9408+000 | 3.9499+000 | -0.23 | 0.00648 | 0.19052 | 0.18956 | 0.00096  |
| 11 | 302.160 | 4.2943+000 | 4.3067+000 | -0.29 | 0.00438 | 0.19208 | 0.19070 | 0.00138  |
| 11 | 303.160 | 4.6053+000 | 4.6158+000 | -0.23 | 0.00299 | 0.19269 | 0.19144 | 0.00125  |
| 11 | 304.150 | 5.0203+000 | 5.0389+000 | -0.37 | 0.00162 | 0.19464 | 0.19214 | 0.00250  |
| 11 | 304.650 | 5.3276+000 | 5.3544+000 | -0.50 | 0.00093 | 0.19659 | 0.19247 | 0.00412  |
| 11 | 305.150 | 5.8663+000 | 5.9127+000 | -0.78 | 0.00025 | 0.20313 | 0.19275 | 0.01038  |

## LABORATORY NOTE

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SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME

R.D. Goodwin

DATE

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Table 17. Calculated oxygen vapor densities.

| T, K    | R, MOL/L   | DR/DT      | D2R/DT2    |
|---------|------------|------------|------------|
| 54.351  | 3.3612-004 | 9.6727-005 | 2.4354-005 |
| 56.000  | 5.3288-004 | 1.4452-004 | 3.4007-005 |
| 58.000  | 8.9941-004 | 2.2709-004 | 4.9253-005 |
| 60.000  | 1.4644-003 | 3.4449-004 | 6.8929-005 |
| 62.000  | 2.3068-003 | 5.0609-004 | 9.3527-005 |
| 64.000  | 3.5251-003 | 7.2213-004 | 1.2342-004 |
| 66.000  | 5.2388-003 | 1.0035-003 | 1.5884-004 |
| 68.000  | 7.5899-003 | 1.3613-003 | 1.9990-004 |
| 70.000  | 1.0742-002 | 1.8068-003 | 2.4655-004 |
| 72.000  | 1.4883-002 | 2.3511-003 | 2.9868-004 |
| 74.000  | 2.0220-002 | 3.0050-003 | 3.5605-004 |
| 76.000  | 2.6983-002 | 3.7786-003 | 4.1840-004 |
| 78.000  | 3.5421-002 | 4.6817-003 | 4.8543-004 |
| 80.000  | 4.5802-002 | 5.7233-003 | 5.5684-004 |
| 82.000  | 5.8412-002 | 6.9118-003 | 6.3239-004 |
| 84.000  | 7.3552-002 | 8.2554-003 | 7.1185-004 |
| 86.000  | 9.1542-002 | 9.7617-003 | 7.9510-004 |
| 88.000  | 1.1271-001 | 1.1438-002 | 8.8208-004 |
| 90.000  | 1.3741-001 | 1.3293-002 | 9.7286-004 |
| 92.000  | 1.6601-001 | 1.5332-002 | 1.0676-003 |
| 94.000  | 1.9887-001 | 1.7566-002 | 1.1666-003 |
| 96.000  | 2.3641-001 | 2.0002-002 | 1.2703-003 |
| 98.000  | 2.7902-001 | 2.2651-002 | 1.3793-003 |
| 100.000 | 3.2716-001 | 2.5523-002 | 1.4944-003 |
| 102.000 | 3.8127-001 | 2.8633-002 | 1.6164-003 |
| 104.000 | 4.4186-001 | 3.1994-002 | 1.7466-003 |
| 106.000 | 5.0943-001 | 3.5626-002 | 1.8865-003 |
| 108.000 | 5.8455-001 | 3.9548-002 | 2.0377-003 |
| 110.000 | 6.6783-001 | 4.3785-002 | 2.2023-003 |
| 112.000 | 7.5992-001 | 4.8368-002 | 2.3830-003 |
| 114.000 | 8.6155-001 | 5.3330-002 | 2.5829-003 |
| 116.000 | 9.7353-001 | 5.8715-002 | 2.8059-003 |
| 118.000 | 1.0967+000 | 6.4572-002 | 3.0569-003 |
| 120.000 | 1.2322+000 | 7.0965-002 | 3.3422-003 |
| 122.000 | 1.3810+000 | 7.7969-002 | 3.6695-003 |
| 124.000 | 1.5445+000 | 8.5678-002 | 4.0493-003 |
| 126.000 | 1.7243+000 | 9.4210-002 | 4.4951-003 |
| 128.000 | 1.9220+000 | 1.0371-001 | 5.0254-003 |
| 130.000 | 2.1399+000 | 1.1438-001 | 5.6657-003 |
| 132.000 | 2.3805+000 | 1.2647-001 | 6.4520-003 |
| 134.000 | 2.6470+000 | 1.4032-001 | 7.4368-003 |
| 136.000 | 2.9433+000 | 1.5641-001 | 8.6997-003 |
| 138.000 | 3.2745+000 | 1.7539-001 | 1.0366-002 |
| 140.000 | 3.6474+000 | 1.9828-001 | 1.2644-002 |
| 142.000 | 4.0712+000 | 2.2661-001 | 1.5903-002 |
| 144.000 | 4.5592+000 | 2.6300-001 | 2.0854-002 |
| 146.000 | 5.1316+000 | 3.1214-001 | 2.9031-002 |
| 148.000 | 5.8225+000 | 3.8373-001 | 4.4334-002 |
| 150.000 | 6.6967+000 | 5.0204-001 | 7.9575-002 |
| 152.000 | 7.9138+000 | 7.5420-001 | 2.0346-001 |
| 154.000 | 1.0230+001 | 2.0822+000 | 2.4109+000 |
| 154.576 | 1.3630+001 | 0.0000+000 | 0.0000+000 |

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R.D. Goodwin

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Table 18. Calculated fluorine vapor densities.

| T, K    | R, MOL/L   | DR/DT      | D2R/DT2    |
|---------|------------|------------|------------|
| 53.481  | 5.6700-004 | 1.6771-004 | 4.2852-005 |
| 54.000  | 6.6001-004 | 1.9119-004 | 4.7718-005 |
| 56.000  | 1.1518-003 | 3.0817-004 | 7.0323-005 |
| 58.000  | 1.9272-003 | 4.7699-004 | 9.9683-005 |
| 60.000  | 3.1038-003 | 7.1188-004 | 1.3650-004 |
| 62.000  | 4.8291-003 | 1.0283-003 | 1.8127-004 |
| 64.000  | 7.2821-003 | 1.4424-003 | 2.3426-004 |
| 66.000  | 1.0675-002 | 1.9709-003 | 2.9554-004 |
| 68.000  | 1.5253-002 | 2.6301-003 | 3.6499-004 |
| 70.000  | 2.1293-002 | 3.4361-003 | 4.4236-004 |
| 72.000  | 2.9105-002 | 4.4046-003 | 5.2731-004 |
| 74.000  | 3.9029-002 | 5.5501-003 | 6.1945-004 |
| 76.000  | 5.1434-002 | 6.8869-003 | 7.1844-004 |
| 78.000  | 6.6713-002 | 8.4282-003 | 8.2395-004 |
| 80.000  | 8.5291-002 | 1.0187-002 | 9.3580-004 |
| 82.000  | 1.0761-001 | 1.2176-002 | 1.0539-003 |
| 84.000  | 1.3416-001 | 1.4407-002 | 1.1783-003 |
| 86.000  | 1.6541-001 | 1.6893-002 | 1.3094-003 |
| 88.000  | 2.0191-001 | 1.9649-002 | 1.4475-003 |
| 90.000  | 2.4420-001 | 2.2689-002 | 1.5935-003 |
| 92.000  | 2.9286-001 | 2.6029-002 | 1.7482-003 |
| 94.000  | 3.4852-001 | 2.9688-002 | 1.9129-003 |
| 96.000  | 4.1184-001 | 3.3688-002 | 2.0893-003 |
| 98.000  | 4.8352-001 | 3.8054-002 | 2.2793-003 |
| 100.000 | 5.6432-001 | 4.2816-002 | 2.4854-003 |
| 102.000 | 6.5507-001 | 4.8009-002 | 2.7105-003 |
| 104.000 | 7.5667-001 | 5.3674-002 | 2.9585-003 |
| 106.000 | 8.7012-001 | 5.9861-002 | 3.2339-003 |
| 108.000 | 9.9651-001 | 6.6631-002 | 3.5426-003 |
| 110.000 | 1.1371+000 | 7.4058-002 | 3.8918-003 |
| 112.000 | 1.2932+000 | 8.2232-002 | 4.2910-003 |
| 114.000 | 1.4666+000 | 9.1264-002 | 4.7523-003 |
| 116.000 | 1.6590+000 | 1.0129-001 | 5.2919-003 |
| 118.000 | 1.8725+000 | 1.1250-001 | 5.9315-003 |
| 120.000 | 2.1099+000 | 1.2511-001 | 6.7013-003 |
| 122.000 | 2.3741+000 | 1.3942-001 | 7.6437-003 |
| 124.000 | 2.6690+000 | 1.5584-001 | 8.8210-003 |
| 126.000 | 2.9992+000 | 1.7492-001 | 1.0328-002 |
| 128.000 | 3.3709+000 | 1.9746-001 | 1.2313-002 |
| 130.000 | 3.7921+000 | 2.2465-001 | 1.5026-002 |
| 132.000 | 4.2739+000 | 2.5834-001 | 1.8913-002 |
| 134.000 | 4.8319+000 | 3.0165-001 | 2.4841-002 |
| 136.000 | 5.4905+000 | 3.6028-001 | 3.4720-002 |
| 138.000 | 6.2909+000 | 4.4628-001 | 5.3532-002 |
| 140.000 | 7.3133+000 | 5.9079-001 | 9.8476-002 |
| 142.000 | 8.7644+000 | 9.1469-001 | 2.7251-001 |
| 144.000 | 1.1893+001 | 3.5620+000 | 7.7289+000 |
| 144.310 | 1.5150+001 | 0.0000+000 | 0.0000+000 |



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## NAME

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## DATE

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Table 19. Calculated methane vapor densities.

| T, K    | R, MOL/L   | DR/DT      | D2R/DT2    |
|---------|------------|------------|------------|
| 90.680  | 1.5679-002 | 1.8523-003 | 1.7385-004 |
| 92.000  | 1.8280-002 | 2.0919-003 | 1.8937-004 |
| 94.000  | 2.2858-002 | 2.4952-003 | 2.1409-004 |
| 96.000  | 2.8294-002 | 2.9492-003 | 2.4020-004 |
| 98.000  | 3.4691-002 | 3.4569-003 | 2.6763-004 |
| 100.000 | 4.2159-002 | 4.0206-003 | 2.9634-004 |
| 102.000 | 5.0813-002 | 4.6430-003 | 3.2628-004 |
| 104.000 | 6.0772-002 | 5.3265-003 | 3.5744-004 |
| 106.000 | 7.2161-002 | 6.0736-003 | 3.8980-004 |
| 108.000 | 8.5110-002 | 6.8866-003 | 4.2339-004 |
| 110.000 | 9.9753-002 | 7.7680-003 | 4.5823-004 |
| 112.000 | 1.1623-001 | 8.7204-003 | 4.9439-004 |
| 114.000 | 1.3468-001 | 9.7465-003 | 5.3195-004 |
| 116.000 | 1.5527-001 | 1.0849-002 | 5.7100-004 |
| 118.000 | 1.7813-001 | 1.2032-002 | 6.1170-004 |
| 120.000 | 2.0345-001 | 1.3297-002 | 6.5420-004 |
| 122.000 | 2.3138-001 | 1.4650-002 | 6.9870-004 |
| 124.000 | 2.6211-001 | 1.6093-002 | 7.4545-004 |
| 126.000 | 2.9582-001 | 1.7633-002 | 7.9471-004 |
| 128.000 | 3.3271-001 | 1.9274-002 | 8.4681-004 |
| 130.000 | 3.7299-001 | 2.1023-002 | 9.0214-004 |
| 132.000 | 4.1687-001 | 2.2885-002 | 9.6113-004 |
| 134.000 | 4.6461-001 | 2.4870-002 | 1.0243-003 |
| 136.000 | 5.1644-001 | 2.6986-002 | 1.0922-003 |
| 138.000 | 5.7264-001 | 2.9242-002 | 1.1657-003 |
| 140.000 | 6.3351-001 | 3.1652-002 | 1.2454-003 |
| 142.000 | 6.9937-001 | 3.4229-002 | 1.3325-003 |
| 144.000 | 7.7055-001 | 3.6988-002 | 1.4280-003 |
| 146.000 | 8.4745-001 | 3.9948-002 | 1.5335-003 |
| 148.000 | 9.3049-001 | 4.3130-002 | 1.6506-003 |
| 150.000 | 1.0201+000 | 4.6559-002 | 1.7815-003 |
| 152.000 | 1.1169+000 | 5.0267-002 | 1.9288-003 |
| 154.000 | 1.2214+000 | 5.4288-002 | 2.0957-003 |
| 156.000 | 1.3343+000 | 5.8665-002 | 2.2865-003 |
| 158.000 | 1.4563+000 | 6.3453-002 | 2.5065-003 |
| 160.000 | 1.5884+000 | 6.8715-002 | 2.7627-003 |
| 162.000 | 1.7316+000 | 7.4534-002 | 3.0643-003 |
| 164.000 | 1.8870+000 | 8.1011-002 | 3.4240-003 |
| 166.000 | 2.0561+000 | 8.8280-002 | 3.8592-003 |
| 168.000 | 2.2408+000 | 9.6514-002 | 4.3945-003 |
| 170.000 | 2.4430+000 | 1.0595-001 | 5.0661-003 |
| 172.000 | 2.6656+000 | 1.1691-001 | 5.9289-003 |
| 174.000 | 2.9119+000 | 1.2985-001 | 7.0695-003 |
| 176.000 | 3.1867+000 | 1.4546-001 | 8.6322-003 |
| 178.000 | 3.4963+000 | 1.6482-001 | 1.0873-002 |
| 180.000 | 3.8497+000 | 1.8973-001 | 1.4288-002 |
| 182.000 | 4.2610+000 | 2.2344-001 | 1.9949-002 |
| 184.000 | 4.7537+000 | 2.7274-001 | 3.0592-002 |
| 186.000 | 5.3730+000 | 3.5464-001 | 5.5251-002 |
| 188.000 | 6.2307+000 | 5.3071-001 | 1.4281-001 |
| 190.000 | 7.8668+000 | 1.4868+000 | 1.7833+000 |
| 190.555 | 1.0200+001 | 0.0000+000 | 0.0000+000 |

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NAME

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Table 20. Calculated ethane vapor densities.

## ETHANE SATURATED VAPOR DENSITIES

| T, K    | R, MOL/L   | DR/DT      | D2R/DT2    |
|---------|------------|------------|------------|
| 89.899  | 1.3511-006 | 3.4418-007 | 7.9422-008 |
| 90.000  | 1.3863-006 | 3.5229-007 | 8.1081-008 |
| 95.000  | 4.5944-006 | 1.0378-006 | 2.1037-007 |
| 100.000 | 1.3356-005 | 2.6924-006 | 4.8256-007 |
| 105.000 | 3.4683-005 | 6.2648-006 | 9.9665-007 |
| 110.000 | 8.1696-005 | 1.3276-005 | 1.8818-006 |
| 115.000 | 1.7684-004 | 2.5955-005 | 3.2903-006 |
| 120.000 | 3.5568-004 | 4.7323-005 | 5.3851-006 |
| 125.000 | 6.7091-004 | 8.1216-005 | 8.3256-006 |
| 130.000 | 1.1963-003 | 1.3223-004 | 1.2254-005 |
| 135.000 | 2.0304-003 | 2.0559-004 | 1.7283-005 |
| 140.000 | 3.2990-003 | 3.0703-004 | 2.3493-005 |
| 145.000 | 5.1575-003 | 4.4257-004 | 3.0926-005 |
| 150.000 | 7.7918-003 | 6.1835-004 | 3.9592-005 |
| 155.000 | 1.1418-002 | 8.4051-004 | 4.9474-005 |
| 160.000 | 1.6284-002 | 1.1151-003 | 6.0539-005 |
| 165.000 | 2.2666-002 | 1.4478-003 | 7.2744-005 |
| 170.000 | 3.0869-002 | 1.8443-003 | 8.6050-005 |
| 175.000 | 4.1225-002 | 2.3101-003 | 1.0043-004 |
| 180.000 | 5.4094-002 | 2.8504-003 | 1.1588-004 |
| 185.000 | 6.9862-002 | 3.4707-003 | 1.3243-004 |
| 190.000 | 8.8944-002 | 4.1767-003 | 1.5014-004 |
| 195.000 | 1.1178-001 | 4.9742-003 | 1.6912-004 |
| 200.000 | 1.3885-001 | 5.8703-003 | 1.8956-004 |
| 205.000 | 1.7066-001 | 6.8727-003 | 2.1170-004 |
| 210.000 | 2.0777-001 | 7.9907-003 | 2.3587-004 |
| 215.000 | 2.5078-001 | 9.2355-003 | 2.6252-004 |
| 220.000 | 3.0036-001 | 1.0621-002 | 2.9224-004 |
| 225.000 | 3.5725-001 | 1.2164-002 | 3.2581-004 |
| 230.000 | 4.2230-001 | 1.3887-002 | 3.6425-004 |
| 235.000 | 4.9647-001 | 1.5817-002 | 4.0894-004 |
| 240.000 | 5.8088-001 | 1.7990-002 | 4.6176-004 |
| 245.000 | 6.7685-001 | 2.0453-002 | 5.2532-004 |
| 250.000 | 7.8599-001 | 2.3267-002 | 6.0330-004 |
| 255.000 | 9.1025-001 | 2.6519-002 | 7.0116-004 |
| 260.000 | 1.0521+000 | 3.0325-002 | 8.2712-004 |
| 265.000 | 1.2147+000 | 3.4858-002 | 9.9430-004 |
| 270.000 | 1.4023+000 | 4.0373-002 | 1.2246-003 |
| 275.000 | 1.6207+000 | 4.7273-002 | 1.5572-003 |
| 280.000 | 1.8784+000 | 5.6239-002 | 2.0691-003 |
| 285.000 | 2.1886+000 | 6.8532-002 | 2.9298-003 |
| 290.000 | 2.5736+000 | 8.6820-002 | 4.5876-003 |
| 295.000 | 3.0777+000 | 1.1813-001 | 8.6241-003 |
| 300.000 | 3.8180+000 | 1.9083-001 | 2.5135-002 |
| 305.000 | 5.6889+000 | 1.2377+000 | 2.4827+000 |
| 305.330 | 6.8700+000 | 0.0000+000 | 0.0000+000 |



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NAME

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## PROGRAM LICKFIT

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C REPRESENT ETHANE SATURATED LIQUID DENSITIES.
C DEFINE X = (TC-T)/(TC-TT), Q = X**1/3, XE = X**E, AND -
C DEFINE YY = (D-DC)/(DT-DC), WHEN THE EQN. IS -
C (YY-X)/(XE-X) = A1 + A2*Q2 + A3*Q3 + . . .
C DCRT = 6.86, 6.87 POSSIBLY VIA MY VAPORDEN EQN.
C DTRP = 21.68 ESTIM. VIA REID C. MILLER.
C ID, (9)TESTER, (10)DOUSLIN, (11)SLIWINSKI, (12)CANFIELD ET AL.,
C ID, (13)KLOSEK, (14)MILLER, (15)EUBANK, (16)TOMLINSON
COMMON E,AZ,TTRP,TCRT,DTRP,DCRT,DRDT,D2RDT2,A(6)
COMMON/999/NP,NF,H(15),Y(200),G(200,15)
DIMENSION ID(99),T(99),DEN(99),U(99),W(99),XQ(99)
1 FORMAT(I5, 2F10.0)
2 FORMAT(1H1 13X 1HE 8X2HAZ 6X4HDCRT 8X2HSS)
3 FORMAT(5X 4F10.3)
4 FORMAT(1H1 17X *ETHANE SATURATED LIQUID DENSITIES, E =* F6.3//
1 20X 6HTCRT =F8.3, 8H, TTRP =F8.4//
2 20X 6HDCRT =F8.3, 8H, DTRP =F8.4// 2(13X 3E15.7//) /
3 8X2HID 7X3HT,K 5X5HMOL/L 6X4HCALC 4X4HPCNT
4 14X 1HX 8X2HYX 8X2HYC 6X4HYDIF )
5 FORMAT(5X I5, 3F10.3, F8.2, F15.5, 3F10.5)
6 FORMAT(1H1 16X *ETHANE SATURATED LIQUID DENSITIES* //
1 17X 3HT,K 3X7HR,MOL/L 5X5HDT/DT 3X7HD2R/DT2 )
7 FORMAT(10X 2F10.3, F10.4, F10.5)
9 FORMAT(18X 4HNP =I3, 10H, RMSPCT =F7.3//

C
C DO ALL FOUR, OXYGEN, FLUORINE, METHANE, AND ETHANE.
10 DO 99 IG=1,4 $ GOTO(11,13,15,17),IG
C CONSTANTS FOR OXYGEN.
11 TTRP=54.3507 $ TCRT=154.576 $ TZ=52 $ DT=2 $ NZ=52
12 DTRP=40.83 $ DCRT=13.63 $ DZ=13.58 $ EZ=0.340 $ GOTO 19
C CONSTANTS FOR FLUORINE.
13 TTRP=53.4811 $ TCRT=144.31 $ TZ=50 $ DT=2 $ NZ=48
14 DTRP=44.6623 $ DCRT=15.15 $ DZ=15.10 $ EZ=0.342 $ GOTO 19
C CONSTANTS FOR METHANE.
15 TTRP=90.680 $ TCRT=190.555 $ TZ=88 $ DT=2 $ NZ=52
16 DTRP=28.147 $ DCRT=10.20 $ DZ=10.05 $ EZ=0.350 $ GOTO 19
C CONSTANTS FOR ETHANE.
17 TTRP=89.899 $ TCRT=305.33 $ TZ=80 $ DT=5 $ NZ=46
18 DTRP=21.68 $ DCRT= 6.87 $ DZ= 6.82 $ EZ=0.349
19 XN = TCRT-TTRP $ YN = DTRP-DCRT
C READ NP DATA FOR LEAST SQUARES.
C READ L.A.WEBER S OXYGEN VOLUMES, CC/MOL.
20 DO 27 J=1,99 $ READ 1, ID(J),T(J),DEN(J) $ IF(ID(J)) 21,28
21 IF(ID(J)-15) 23,22
22 CONTINUE
23 IF(ID(J)-99) 25,24
24 DEN(J) = 1000/DEN(J)
25 U(J) = X = (TCRT-T(J))/XN $ Q = CUBERTF(X) $ DO 26 K=2,6
26 G(J,K) = Q**K $ G(J,1) = 1
27 W(J) = (DEN(J)-DCRT)/YN
28 NPP = NP = J-1 $ NF = 3 $ E = 0.36
C EXPLORE E, AZ, AND DCRT.
29 AZ = NF $ SSK = 1.0E+010
30 DO 49 IE=1,21 $ E = EZ + 0.001*IE

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C SET UP THE LEAST SQUARES ARRAYS.

```

36 DO 40 J=1,NP $ X = U(J) $ XQ(J) = XE = X**E
37 Y(J) = (W(J)-X)/(XE-X)
40 CONTINUE $ CALL EGENFT $ SS=0 $ DO 43 J=1,NP $ YC=0 $ DO 41 K=1,NF
41 YC = YC + H(K)*G(J,K) $ X = U(J) $ XE = XQ(J)
42 DC = DCRT + (X + (XE-X)*YC)*YN
43 SS = SS + (DEN(J)/DC-1)**2 $ SS = 100*SQRTF(SS/NP)
44 IF(SS.LT.SSK) 45,48
45 SSK=SS $ EK=E $ AZK=AZ $ DK=DCRT
46 DO 47 K=1,6
47 A(K) = H(K)
48 CONTINUE
49 CONTINUE
50 E=EK $ AZ=AZK $ DCRT=DK $ YN = DTRP - DCRT

```

C USE SAVED CONSTANTS FOR DEVIATIONS.

```

60 PRINT 4, E, TCRT, TTRP, DCRT, DTRP, (A(K), K=1,6) $ SS = 0
61 DO 70 J=1,NPP $ X = U(J) $ XE = X**E $ XEX = XE-X
62 YC = 0 $ DO 63 K=1,NF
63 YC = YC + A(K)*G(J,K)
64 YS = X + XEX*YC $ DC = DCRT + YN*YS
65 YX = (W(J)-X)/XEX $ YD = YX-YC
66 PCT = 100*(DEN(J)/DC-1) $ SS = SS + PCT**2
67 PRINT 5, ID(J), T(J), DEN(J), DC, PCT, X, YX, YC, YD
68 IF(J-NP) 70,69
69 SS = SQRTF(SS/NP) $ PRINT 9, NP, SS
70 CONTINUE

```

C PRINT UNIFORM TABLE FOR PUBLICATION.

```

71 PRINT 6 $ DO 80 J=1,NZ $ IF(J-1) 73,72
72 TT = TTRP $ GO TO 76
73 IF(J-NZ) 75,74
74 TT = TCRT $ GO TO 76
75 TT = TZ + DT*J
76 R = DENLIQF(TT)
80 PRINT 7, TT, R, DROT, D2ROT2
99 CONTINUE

```

C DO OTHER ETHANE DATA WITH EXISTING COEFFICIENTS.

```

100 PRINT 4, E, TCRT, TTRP, DCRT, DTRP, (A(K), K=1,6) $ SS = 0
101 DO 110 J=1,99 $ READ 1, IDD, TT, DN $ IF(IDD) 102,999
102 X=(TCRT-TT)/XN $ Q=CUBERTF(X) $ XE=X**E $ XEX=XE-X
103 YC = A(1) $ DO 104 K=2,NF
104 YC = YC + A(K)*Q**K
105 DC = DCRT + YN*(X+XEX*YC) $ PCT = 100*(DN/DC-1)
106 YY = (DN-DCRT)/YN $ YX = (YY-X)/XEX $ YD = YX-YC
110 PRINT 5, IDD, TT, DN, DC, PCT, X, YX, YC, YD
999 STOP $ END

```

## LABORATORY NOTE

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SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME

R.D. Goodwin

DATE

Sept. 18, 1973

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## PROGRAM VAPORFIT

```

C REPRESENT ETHANE SATURATED VAPOR DENSITIES.
C THIS FORM IS CONSTRAINED AT THE TRIPLE POINT, AND
C DEFINE X(T) AS FOR THE VAPOR PRESSURE EQUATION -
C  $Z = (1-X) = (TC/T-1)/(TC/TT-1)$ ,  $ZE = Z**E$ ,  $Q = Z**1/3$ , AND -
C DEFINE YY =  $LN(DC/D)/LN(DC/DT)$ , AND THE DEPENDENT VARIABLE -
C  $Y(Z,YY) = (YY-Z)/(ZE-Z)$ , WHEN THE L.S. EQN. IS -
C  $Y(Z,YY) = A1 + A2*Q2 + A3*Q3 + A4*Q4 + . . .$ 
C ID., (1)VIRIAL/V.P., (6)PORTER, (10)DOUSLIN, (11)SLIWINSKI.
C COMMON E,AL, TTRP,TCRT, DTRP,DCRT, DROT,D2ROT2, A(9)
C COMMON/999/NP,NF,H(15),Y(200),G(200,15)
C DIMENSION ID(99),T(99),DEN(99), U(99),W(99), ZQ(99)
1 FORMAT(I5, F10.0, E15.5)
2 FORMAT(1H1 18X 1HE 8X2HAL 6X4HDCRT 8X2HSS)
3 FORMAT(10X 4F10.3)
4 FORMAT(1H1 17X *ETHANE SATURATED VAPOR DENSITIES, E =* F6.3//
1 20X 6HTCRT =F8.3, 8H, TTRP =F8.4/
2 20X 6HDCRT =F8.3, 8H, DTRP =E12.5// 2(13X 4E15.7//) /
2 8X2HID 7X3HT,K 8X5HMOL/L 8X5HCALCD 4X4HPCNT
3 12X 1HZ 8X2HYX 8X2HYC 6X4HYDIF )
5 FORMAT(5X I5, F10.3, 2E13.4, F8.2, F13.5, 3F10.5)
6 FORMAT(I5, 2F10.0)
7 FORMAT(1H1 16X *ETHANE SATURATED VAPOR DENSITIES* //
1 17X 3HT,K 6X7HR,MOL/L 8X5HDCRT/DT 6X7HDCRT/DT2 )
8 FORMAT(10X F10.3, 3E13.4)
9 FORMAT(18X 4HNP =I3, 10H, RMSPCT =F7.3//)
61 FORMAT(1H1 7X2HID 7X3HT,K 8X5HMOL/L 8X5HCALCD 4X4HPCNT
1 12X 1HZ 8X2HYX 8X2HYC 6X4HYDIF )

C
C DO ALL FOUR, OXYGEN, FLUORINE, METHANE, ETHANE.
10 DO 81 IG=1,4 $ GOTO(11,13,15,17),IG
C CONSTANTS FOR OXYGEN.
11 TTRP=54.3507 $ TCRT=154.576 $ TZ=52 $ DT=2 $ NZ=52
12 DTRP=3.36122E-4 $ DCRT=13.63 $ DZ=13.58 $ EZ=0.360 $ GOTO 19
C CONSTANTS FOR FLUORINE.
13 TTRP=53.4811 $ TCRT=144.31 $ TZ=50 $ DT=2 $ NZ=48
14 DTRP=5.670E-4 $ DCRT=15.15 $ DZ=15.10 $ EZ=0.340 $ GOTO 19
C CONSTANTS FOR METHANE.
15 TTRP=90.680 $ TCRT=190.555 $ TZ=88 $ DT=2 $ NZ=52
16 DTRP=0.01567865 $ DCRT=10.20 $ DZ=10.05 $ EZ=0.360 $ GOTO 19
C CONSTANTS FOR ETHANE.
C OMIT 24, AND FIX DTRP.
17 TTRP=89.899 $ TCRT=305.33 $ TZ=80 $ DT=5 $ NZ=46
18 DTRP= 1.35114E-6 $ DCRT=6.87 $ DZ=6.84 $ EZ=0.340
19 ZN = TCRT/TTRP-1 $ YN = LOGF(DCRT/DTRP)
C READ OUR ID(1) DATA MIXED WITH DOUSLIN.
C INCREASE OUR DEN BY 0.15 PCT TO AGREE WITH DOUSLIN.
20 DO 27 J=1,200 $ IF(IG-4) 22,21
21 READ 1, ID(J),T(J),DEN(J) $ IF(ID(J)) 23,28
22 READ 6, ID(J),T(J),DEN(J) $ IF(ID(J)) 25,28
23 IF(ID(J)-1) 25,24
24 CONTINUE
25 U(J) = Z = (TCRT/T(J)-1)/ZN $ Q = CUBERTF(Z) $ DO 26 K=2,7
26 G(J,K) = Q**K $ G(J,1) = 1
27 W(J) = LOGF(DCRT/DEN(J))/YN

```



## LABORATORY NOTE

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## VAPORFIT

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```

28 NP = J-1 $ AL = NF = 5 $ E = 0.360
C   EXPLORE DCRT, AND EXPONENT E.
33 SSK = 1.0E+010
34 DO 48 IE=1,21 $ E = EZ + 0.002*IE
C   SET UP THE ARRAYS FOR LEAST SQUARES.
36 DO 39 J=1,NP $ Z = U(J) $ ZQ(J) = ZE = Z**E
37 Y(J) = (W(J)-Z)/(ZE-Z)
39 CONTINUE $ CALL EGENFT $ SS = 0
C   NOW GET THE RMS DEVIATION.
40 DO 44 J=1,NP $ YC = 0 $ DO 41 K=1,NF
41 YC = YC + H(K)*G(J,K)
42 Z = U(J) $ YS = Z + (ZQ(J)-Z)*YC
43 DC = DCRT*EXPF(-YN*YS)
44 SS = SS + (DC/DEN(J)-1)**2 $ SS = 100*SQRTF(SS/NP)
45 IF(SS.LT.SSK) 46,48
46 SSK=SS $ EK=E $ ALK=AL $ DK=DCRT $ DO 47 K=1,9
47 A(K) = H(K)
48 CONTINUE
49 E=EK $ AL=ALK $ DCRT=DK $ YN = LOGF(DK/DTRP)
C   USE SAVED CONSTANTS FOR DEVIATIONS.
50 PRINT 4, E, TCRT, TTRP, DCRT, DTRP, (A(K),K=1,8) $ SS = 0
51 DO 59 J=1,NP $ Z = U(J) $ ZE = Z**E $ ZEZ = ZE - Z
52 YC = 0 $ DO 53 K=1,NF
53 YC = YC + A(K)*G(J,K)
54 YS = Z + ZEZ*YC $ DC = DCRT*EXPF(-YN*YS)
55 YX = (W(J)-Z)/ZEZ $ YD = YX - YC
56 PCT = 100*(DEN(J)/DC-1) $ SS = SS + PCT**2
57 IF(IG.EQ.3.AND.J.EQ.48) 58,59
58 PRINT 61
59 PRINT 5, ID(J), T(J), DEN(J), DC, PCT, Z, YX, YC, YD
60 SS = SQRTF(SS/NP) $ PRINT 9, NP, SS
C   PRINT UNIFORM TABLE FOR PUBLICATION.
71 PRINT 7 $ DO 80 J=1,NZ $ IF(J-1) 73,72
72 TT = TTRP $ GO TO 76
73 IF(J-NZ) 75,74
74 TT = TCRT $ GO TO 76
75 TT = TZ + DT*J
76 R = DENGASF(TT)
80 PRINT 8, TT, R, DRDT, D2RDT2
81 CONTINUE $ PRINT 61
C   DO OTHER ETHANE DATA WITH EXISTING COEFFICIENTS.
82 DO 88 J=1,99 $ READ 6, IDD, TT, DN $ IF(IDD) 83,99
83 Z = (TCRT/TT-1)/ZN $ ZE = Z**E $ ZEZ = ZE - Z
84 Q = CUBERTF(Z) $ YC = A(1) $ DO 85 K=2,NF
85 YC = YC + A(K)*Q**K
86 YY = LOGF(DCRT/DN)/YN $ YX = (YY-Z)/ZEZ $ YD = YX-YC
87 DC = DCRT*EXPF(-YN*(Z+ZEZ*YC)) $ PCT = 100*(DN/DC-1)
88 PRINT 5, IDD, TT, DN, DC, PCT, Z, YX, YC, YD
99 STOP $ END

```

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SUBJECT

The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME

R.D. Goodwin

DATE

Sept. 18, 1973

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## FUNCTION DENLIQF(T)

```

C   ETHANE SATURATED LIQUID DENSITIES, MOL/L.
C   Y = A1 + A2*Q2 + A3*Q3 + . . . ,   YN = DTRP-DCRT,
C   DEN = DCRT + YN*(X + (XE-X)*Y).
      COMMON E,AZ,TTRP,TCRT,DTRP,DCRT,DRDT,D2RDT2,A(6)
1  FORMAT(1H0 9X *DENLIQF = 0, T EXCEEDS TCRT. * / )
2  IF(TCRT-T) 3,4,5
3  PRINT 1 $ STOP
4  DENLIQF=DCRT $ DRDT=D2RDT2=0 $ RETURN
5  XN=TCRT-TTRP $ YN=DTRP-DCRT $ X=(TCRT-T)/XN $ DXDT=-1/XN
6  XE = X**E $ XE1 = E*XE/X $ XE2 = (E-1)*XE1/X
7  W = CUBERTF(X) $ W1 = W/3/X $ W2 = -2*W1/3/X
8  Q = XE-X $ Q1 = XE1 - 1 $ Q2 = XE2
9  NF = AZ $ Y = A(1) $ Y1 = Y2 = 0 $ DO 11 K=2,NF
10 Y = Y + A(K)*W**K $ Y1 = Y1 + K*A(K)*W**(K-1)
11 Y2 = Y2 + K*(K-1)*A(K)*W**(K-2)
12 Y2 = Y1*W2 + Y2*W1**2 $ Y1 = Y1*W1
13 DENLIQF = DCRT + (X + Q*Y)*YN
14 DRDT = (1 + Q*Y1 + Q1*Y)*YN*DXDT
15 D2RDT2 = (Q*Y2 + 2*Q1*Y1 + Q2*Y)*YN*DXDT**2 $ RETURN $ END

```

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## FUNCTION DENGASF(T)

```

C   ETHANE SATURATED VAPOR DENSITIES, MOL/L.
C   Y = A1 + A2*Q2 + A3*Q3 + . . . ,   NF = AL,   YN = LN(DCRT/DTRP),
C   U = Z + (ZE-Z)*Y,   DEN = DCRT*EXP(-YN*U).
C   NOTE THAT Z = 0 ONLY AT T = TCRT, WHICH IS EXCLUDED.
      COMMON E,AL,TTRP,TCRT,DTRP,DCRT,DRDT,D2RDT2,A(9)
1  FORMAT(1H0 9X *DENGASF = 0, T EXCEEDS TCRT. * / )
2  IF(TCRT-T) 3,4,5
3  PRINT 1 $ STOP
4  DENGASF = DCRT $ DRDT = D2RDT2 = 0 $ RETURN
5  ZN=TCRT/TTRP-1 $ YN=LOGF(DCRT/DTRP) $ Z=(TCRT/T-1)/ZN
6  DZDT = -TCRT/ZN/T**2 $ D2ZDT2 = -2*DZDT/T
7  ZE = Z**E $ ZE1 = E*ZE/Z $ ZE2 = (E-1)*ZE1/Z
8  X = ZE-Z $ X1 = ZE1 - 1 $ X2 = ZE2
9  Q = CUBERTF(Z) $ Q1 = Q/3/Z $ Q2 = -2*Q1/3/Z
10 NF = AL $ Y = A(1) $ Y1 = Y2 = 0 $ DO 13 K=2,NF
11 Y = Y + A(K)*Q**K
12 Y1 = Y1 + K*A(K)*Q**(K-1)
13 Y2 = Y2 + K*(K-1)*A(K)*Q**(K-2)
14 Y2 = Y1*Q2 + Y2*Q1**2 $ Y1 = Y1*Q1
15 U = Z + X*Y $ UA = 1 + X*Y1 + X1*Y $ U1 = UA*DZDT
16 U2 = UA*D2ZDT2 + (X*Y2 + 2*X1*Y1 + X2*Y)*DZDT**2
17 XP = EXPF(-YN*U) $ DENGASF = F = DCRT*XP $ YU = -YN*U1
18 DRDT = YU*F $ D2RDT2 = (YU*YU-YN*U2)*F $ RETURN $ END

```

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## APPENDIX M

## LABORATORY NOTE

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## SUBJECT

Liquid-Vapor Saturation (Orthobaric) Temperatures of  
Ethane and Methane

NAME R. D. Goodwin

DATE Nov. 28, 1973

1. Introduction.

The present, new investigation has been necessary to accommodate the extreme range of ethane saturated vapor densities (a factor of  $10^7$ ). Our previous work on ethane appears in Lab. Notes 73-2, 3, 4, 5.

Analytical description of the two-phase, liquid-vapor equilibrium (temperature-density relationship) is needed for our new equation of state which originates on this locus (NBS IR 73-342). In particular, the forms used below give the important property that all derivatives are zero at the critical point.

In the following we split the range, using different functions according to  $\rho \leq \rho_c$ . In each case the dependent variable is

$$Y(T) \equiv (T_c / T - 1) / (T_c / T_t - 1) \quad (1)$$

The symbols used here appear in a LIST.

2. The Saturated Vapor Temperatures.

The analytical formulation is

$$Y(T) = U(\sigma) \cdot [1 + A_0 \cdot \ln(\sigma / \sigma_g) + W(\sigma)] \quad (2)$$

where

$$U(\sigma) \equiv \exp[\alpha \cdot (u_g - u)], \quad (2-a)$$

and

$$W(\sigma) = \sum_{i=1}^n A_i \cdot (q^i - q_g^i). \quad (2-b)$$

The notation is  $q = \sigma^{1/3}$ ,  $q_g = \sigma_g^{1/3}$ , and  $u_g \equiv 1 / |\sigma_g - 1|$ .

This equation is constrained at the vapor triple point.

Fixed-point constants are given by table 1, and coefficients by table 2. The comparisons of results for ethane and for methane are in tables 3, 5. Deviations necessarily are systematic because the "data" are smoothed analytically (Lab. Note 73-5). We believe all deviations to be well within the real accuracy of the data.

3. The Saturated Liquid Temperatures.

The analytical formulation is

$$\ln(Y) = \beta \cdot (u_t - u) + W(\sigma) \quad (3)$$

where

$$W(\sigma) = \sum_{i=1}^n B_i \cdot (x^i - x_t^i). \quad (3-a)$$

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## SUBJECT

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Ethane and Methane

NAME R. D. Goodwin

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The notation is  $x_t \equiv |\sigma_t - 1|$ ,  $u_t \equiv 1/x_t$ .

This equation is constrained at the liquid triple point.

The comparisons of results for ethane and for methane are in tables 4, 6. Computer programs are attached.

## LIST OF SYMBOLS

|              |                                                                            |      |
|--------------|----------------------------------------------------------------------------|------|
| $d$ ,        | density, mol/l,                                                            | DEN  |
| $d_c$ ,      | critical-point density,                                                    | DCRT |
| $d_g$ ,      | vapor triple-point density,                                                | DGAT |
| $d_t$ ,      | liquid triple-point density,                                               | DTRP |
| $q$ ,        | $\sigma^{1/3}$ , $q_g \equiv \sigma_g^{1/3}$                               |      |
| $\rho$ ,     | $d/d_t$ , density reduced at liquid triple point                           |      |
| $\sigma$ ,   | $d/d_c$ , density reduced at the critical point                            |      |
| $\sigma_g$ , | $d_g/d_c$ , reduced triple-point vapor density                             |      |
| $\sigma_t$ , | $d_t/d_c$ , reduced triple-point liquid density                            |      |
| $T$ ,        | $T_s(\rho)$ , the saturation temperature                                   |      |
| $T_c$ ,      | critical-point temperature,                                                | TCRT |
| $T_t$ ,      | triple-point temperature,                                                  | TTRP |
| $u$ ,        | $1/x$ , $u_g \equiv 1/x_g$ , $u_t \equiv 1/x_t$                            |      |
| $x$ ,        | $ \sigma - 1 $ , $x_g \equiv  \sigma_g - 1 $ , $x_t \equiv  \sigma_t - 1 $ |      |

Table 1. The fixed-point constants

|                | <u>Ethane</u>           | <u>Methane</u>             |
|----------------|-------------------------|----------------------------|
| $T_t$ , K      | 89.899                  | 90.680                     |
| $T_c$ , K      | 305.330                 | 190.555                    |
| $d_c$ , mol/l  | 6.87                    | 10.20                      |
| $d_t$ , liquid | 21.68                   | 28.147                     |
| $d_g$ , vapor  | $1.35114 \cdot 10^{-6}$ | $1.567\ 865 \cdot 10^{-2}$ |

## LABORATORY NOTE

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## SUBJECT

Liquid-Vapor Saturation (Orthobaric) Temperatures of  
Ethane and Methane

## NAME

R. D. Goodwin

## DATE

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Table 2. Coefficients for the equations

|               |          | <u>Ethane</u> | <u>Methane</u> |
|---------------|----------|---------------|----------------|
| <u>Vapor</u>  | $\alpha$ | 3/2           | 1/2            |
|               | $A_0$    | -0.0610 6983  | -0.1596 5159   |
|               | $A_1$    | -0.5510 7806  | -0.6669 5380   |
|               | $A_2$    | 1.8906 0757   | 1.0242 2995    |
|               | $A_3$    | -4.8476 0684  | -0.5885 7993   |
|               | $A_4$    | 8.5887 8625   | 0.2042 8358    |
|               | $A_5$    | -8.3103 1296  | -              |
|               | $A_6$    | 3.3001 3887   | -              |
| <hr/>         |          |               |                |
| rms, %        | d        | 0.111         | 0.043          |
|               | T        | 0.009         | 0.004          |
| <hr/>         |          |               |                |
| <u>Liquid</u> | $\beta$  | 1/3           | 1/3            |
|               | $B_1$    | 9.1071 7170   | 8.5837 7917    |
|               | $B_2$    | -7.9603 9387  | -7.0525 4699   |
|               | $B_3$    | 4.8472 6284   | 4.1610 2443    |
|               | $B_4$    | -1.5919 0104  | -1.3691 9291   |
|               | $B_5$    | 0.2253 7899   | 0.2067 1342    |
| <hr/>         |          |               |                |
| rms, %        | d        | 0.004         | 0.006          |
|               | T        | 0.016         | 0.006          |



|                                                       |  |                    |         |      |
|-------------------------------------------------------|--|--------------------|---------|------|
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| LABORATORY NOTE                                       |  | 2750364            | 73-6    | 4    |
| Subj: Table 3. Ethane Saturated Vapor Temperatures    |  | NAME R. D. Goodwin |         |      |
|                                                       |  | DATE Nov. 28 1973  |         |      |

NF = 7, AL = 1.500, PE = 0.000, DGAT = 1.35114-006

TTRP = 89.899, TCRT = 305.330, DTRP = 21.680, DCRT = 6.870

|             |             |            |             |
|-------------|-------------|------------|-------------|
| -0.06106983 | -0.55107806 | 1.89060757 | -4.84760654 |
| 8.58878625  | -8.31031296 | 3.30013887 | 0.00000000  |
| 0.00000000  | 0.00000000  | 0.00000000 | 0.00000000  |

| MOL/L       | CALC        | PCNT  | T,K     | CALC    | PCNT  | DTS/DC    |
|-------------|-------------|-------|---------|---------|-------|-----------|
| 1.35114-006 | 1.35114-006 | 0.00  | 89.899  | 89.899  | 0.00  | 2.915+006 |
| 1.38631-006 | 1.38619-006 | -0.01 | 90.000  | 90.000  | 0.00  | 2.848+006 |
| 4.59443-006 | 4.58134-006 | -0.28 | 95.000  | 95.013  | 0.01  | 9.651+005 |
| 1.33551-005 | 1.33129-005 | -0.32 | 100.000 | 100.016 | 0.02  | 3.714+005 |
| 3.46326-005 | 3.46067-005 | -0.22 | 105.000 | 105.012 | 0.01  | 1.594+005 |
| 8.16960-005 | 8.16454-005 | -0.06 | 110.000 | 110.004 | 0.00  | 7.518+004 |
| 1.76844-004 | 1.76987-004 | 0.08  | 115.000 | 114.995 | -0.00 | 3.346+004 |
| 3.55631-004 | 3.56292-004 | 0.17  | 120.000 | 119.987 | -0.01 | 2.111+004 |
| 6.70003-004 | 6.72259-004 | 0.20  | 125.000 | 124.983 | -0.01 | 1.231+004 |
| 1.19634-003 | 1.19845-003 | 0.18  | 130.000 | 129.984 | -0.01 | 7.567+003 |
| 2.03041-003 | 2.03275-003 | 0.12  | 135.000 | 134.969 | -0.01 | 4.370+003 |
| 3.29903-003 | 3.30029-003 | 0.04  | 140.000 | 139.996 | -0.00 | 3.262+003 |
| 5.15754-003 | 5.15568-003 | -0.04 | 145.000 | 145.004 | 0.00  | 2.263+003 |
| 7.79177-003 | 7.78449-003 | -0.09 | 150.000 | 150.012 | 0.01  | 1.619+003 |
| 1.14133-002 | 1.14040-002 | -0.13 | 155.000 | 155.017 | 0.01  | 1.191+003 |
| 1.62342-002 | 1.62628-002 | -0.13 | 160.000 | 160.019 | 0.01  | 8.969+002 |
| 2.26660-002 | 2.26402-002 | -0.11 | 165.000 | 165.018 | 0.01  | 6.903+002 |
| 3.08686-002 | 3.08446-002 | -0.08 | 170.000 | 170.013 | 0.01  | 5.415+002 |
| 4.12247-002 | 4.12114-002 | -0.03 | 175.000 | 175.006 | 0.00  | 4.322+002 |
| 5.40339-002 | 5.41016-002 | 0.01  | 180.000 | 179.997 | -0.00 | 3.502+002 |
| 6.98623-002 | 6.99003-002 | 0.05  | 185.000 | 184.989 | -0.01 | 2.877+002 |
| 8.89439-002 | 8.90172-002 | 0.08  | 190.000 | 189.982 | -0.01 | 2.392+002 |
| 1.11782-001 | 1.11888-001 | 0.10  | 195.000 | 194.979 | -0.01 | 2.009+002 |
| 1.38350-001 | 1.38978-001 | 0.09  | 200.000 | 199.978 | -0.01 | 1.704+002 |
| 1.70662-001 | 1.70787-001 | 0.07  | 205.000 | 204.982 | -0.01 | 1.457+002 |
| 2.07770-001 | 2.07862-001 | 0.04  | 210.000 | 209.988 | -0.01 | 1.253+002 |
| 2.56780-001 | 2.50803-001 | 0.01  | 215.000 | 214.997 | -0.00 | 1.085+002 |
| 3.00359-001 | 3.00280-001 | -0.03 | 220.000 | 220.007 | 0.00  | 9.434+001 |
| 3.57253-001 | 3.57050-001 | -0.06 | 225.000 | 225.017 | 0.01  | 9.234+001 |
| 4.22301-001 | 4.21977-001 | -0.08 | 230.000 | 230.023 | 0.01  | 7.208+001 |
| 4.96469-001 | 4.96061-001 | -0.08 | 235.000 | 235.026 | 0.01  | 6.322+001 |
| 5.80877-001 | 5.80460-001 | -0.07 | 240.000 | 240.023 | 0.01  | 5.553+001 |
| 6.76852-001 | 6.76541-001 | -0.05 | 245.000 | 245.015 | 0.01  | 4.379+001 |
| 7.85990-001 | 7.85922-001 | -0.01 | 250.000 | 250.003 | 0.00  | 4.286+001 |
| 9.10251-001 | 9.10553-001 | 0.03  | 255.000 | 254.989 | -0.00 | 3.760+001 |
| 1.05210+000 | 1.05283+000 | 0.07  | 260.000 | 259.976 | -0.01 | 3.291+001 |
| 1.21471+000 | 1.21579+000 | 0.09  | 265.000 | 264.969 | -0.01 | 2.867+001 |
| 1.40231+000 | 1.40343+000 | 0.08  | 270.000 | 269.972 | -0.01 | 2.482+001 |
| 1.62073+000 | 1.62131+000 | 0.04  | 275.000 | 274.988 | -0.00 | 2.124+001 |
| 1.87345+000 | 1.87773+000 | -0.04 | 280.000 | 280.013 | 0.00  | 1.788+001 |
| 2.18360+000 | 2.18618+000 | -0.11 | 285.000 | 285.035 | 0.01  | 1.463+001 |
| 2.57357+000 | 2.57081+000 | -0.11 | 290.000 | 290.032 | 0.01  | 1.146+001 |
| 3.07773+000 | 3.08011+000 | 0.08  | 295.000 | 294.980 | -0.01 | 8.351+000 |
| 3.81303+000 | 3.82168+000 | 0.10  | 300.000 | 299.980 | -0.01 | 5.426+000 |

NP = 44, DNRMSPT = 0.111, TSRMSPT = 0.009

|                                                                                 |  |                    |         |      |
|---------------------------------------------------------------------------------|--|--------------------|---------|------|
| Cryogenics Division-NBS Institute for Basic Standards                           |  | COST CENTER        | FILE NO | PAGE |
| LABORATORY NOTE                                                                 |  | 2750364            | 73-6    | 5    |
| SUBJECT Liquid-Vapor Saturation (Orthobaric) Temperatures of Ethane and Methane |  | NAME R. D. Goodwin |         |      |
|                                                                                 |  | DATE Nov. 28, 1973 |         |      |

Table 4. Ethane Saturated Liquid Temperatures

NF = 5, AL = 0.000, BE = 0.333, OGAT = 1.35114-006

TTRP = 89.899, TCRT = 305.330, DTRP = 21.680, DCRT = 6.870

|            |             |            |             |
|------------|-------------|------------|-------------|
| 9.10717170 | -7.96039387 | 4.84726284 | -1.59190104 |
| 0.22537899 | 0.00000000  | 0.00000000 | 0.00000000  |
| 0.00000000 | 0.00000000  | 0.00000000 | 0.00000000  |

| MOL/L       | CALC        | PCNT  | T, K    | CALC    | PCNT  | DTS/DO     |
|-------------|-------------|-------|---------|---------|-------|------------|
| 2.16800+001 | 2.16800+001 | 0.00  | 89.899  | 89.899  | 0.00  | -2.753+001 |
| 2.16764+001 | 2.16763+001 | -0.00 | 90.000  | 89.999  | -0.00 | -2.753+001 |
| 2.14963+001 | 2.14951+001 | -0.01 | 95.000  | 94.967  | -0.04 | -2.764+001 |
| 2.13162+001 | 2.13145+001 | -0.01 | 100.000 | 99.952  | -0.05 | -2.771+001 |
| 2.11359+001 | 2.11341+001 | -0.01 | 105.000 | 104.951 | -0.05 | -2.773+001 |
| 2.09553+001 | 2.09538+001 | -0.01 | 110.000 | 109.958 | -0.04 | -2.771+001 |
| 2.07743+001 | 2.07732+001 | -0.01 | 115.000 | 114.969 | -0.03 | -2.766+001 |
| 2.05928+001 | 2.05921+001 | -0.00 | 120.000 | 119.983 | -0.01 | -2.758+001 |
| 2.04106+001 | 2.04105+001 | -0.00 | 125.000 | 124.997 | -0.00 | -2.746+001 |
| 2.02276+001 | 2.02260+001 | 0.00  | 130.000 | 130.010 | 0.01  | -2.733+001 |
| 2.00438+001 | 2.00445+001 | 0.00  | 135.000 | 135.020 | 0.01  | -2.717+001 |
| 1.98598+001 | 1.98598+001 | 0.01  | 140.000 | 140.027 | 0.02  | -2.698+001 |
| 1.96727+001 | 1.96739+001 | 0.01  | 145.000 | 145.031 | 0.02  | -2.678+001 |
| 1.94852+001 | 1.94864+001 | 0.01  | 150.000 | 150.032 | 0.02  | -2.655+001 |
| 1.92961+001 | 1.92972+001 | 0.01  | 155.000 | 155.031 | 0.02  | -2.631+001 |
| 1.91052+001 | 1.91062+001 | 0.01  | 160.000 | 160.027 | 0.02  | -2.604+001 |
| 1.89123+001 | 1.89132+001 | 0.00  | 165.000 | 165.021 | 0.01  | -2.575+001 |
| 1.87173+001 | 1.87178+001 | 0.00  | 170.000 | 170.014 | 0.01  | -2.544+001 |
| 1.85198+001 | 1.85201+001 | 0.00  | 175.000 | 175.006 | 0.00  | -2.511+001 |
| 1.83196+001 | 1.83195+001 | -0.00 | 180.000 | 179.999 | -0.00 | -2.476+001 |
| 1.81164+001 | 1.81160+001 | -0.00 | 185.000 | 184.992 | -0.00 | -2.438+001 |
| 1.79098+001 | 1.79092+001 | -0.00 | 190.000 | 189.986 | -0.01 | -2.397+001 |
| 1.76996+001 | 1.76987+001 | -0.00 | 195.000 | 194.981 | -0.01 | -2.354+001 |
| 1.74852+001 | 1.74843+001 | -0.01 | 200.000 | 199.978 | -0.01 | -2.308+001 |
| 1.72664+001 | 1.72653+001 | -0.01 | 205.000 | 204.977 | -0.01 | -2.260+001 |
| 1.70425+001 | 1.70415+001 | -0.01 | 210.000 | 209.979 | -0.01 | -2.208+001 |
| 1.68130+001 | 1.68121+001 | -0.01 | 215.000 | 214.981 | -0.01 | -2.153+001 |
| 1.65774+001 | 1.65767+001 | -0.00 | 220.000 | 219.985 | -0.01 | -2.094+001 |
| 1.63348+001 | 1.63344+001 | -0.00 | 225.000 | 224.990 | -0.00 | -2.033+001 |
| 1.60845+001 | 1.60843+001 | -0.00 | 230.000 | 229.996 | -0.00 | -1.967+001 |
| 1.58255+001 | 1.58256+001 | 0.00  | 235.000 | 235.002 | 0.00  | -1.898+001 |
| 1.55567+001 | 1.55571+001 | 0.00  | 240.000 | 240.007 | 0.00  | -1.825+001 |
| 1.52767+001 | 1.52773+001 | 0.00  | 245.000 | 245.011 | 0.00  | -1.749+001 |
| 1.49838+001 | 1.49846+001 | 0.01  | 250.000 | 250.013 | 0.01  | -1.668+001 |
| 1.46761+001 | 1.46770+001 | 0.01  | 255.000 | 255.014 | 0.01  | -1.582+001 |
| 1.43511+001 | 1.43518+001 | 0.01  | 260.000 | 260.012 | 0.00  | -1.493+001 |
| 1.40054+001 | 1.40059+001 | 0.00  | 265.000 | 265.008 | 0.00  | -1.398+001 |
| 1.36348+001 | 1.36350+001 | 0.00  | 270.000 | 270.002 | 0.00  | -1.298+001 |
| 1.32333+001 | 1.32331+001 | -0.00 | 275.000 | 274.997 | -0.00 | -1.191+001 |
| 1.27923+001 | 1.27917+001 | -0.00 | 280.000 | 279.994 | -0.00 | -1.076+001 |
| 1.22965+001 | 1.22978+001 | -0.01 | 285.000 | 284.993 | -0.00 | -9.500+000 |
| 1.17293+001 | 1.17290+001 | -0.00 | 290.000 | 289.997 | -0.00 | -8.090+000 |
| 1.10398+001 | 1.10403+001 | 0.00  | 295.000 | 295.003 | 0.00  | -6.441+000 |
| 1.01117+001 | 1.01117+001 | 0.00  | 300.000 | 300.000 | -0.00 | -4.358+000 |

NP = 44, DNRMSPT = 0.004, TSRMSPT = 0.016

Table 5. Methane Saturated Vapor Temperatures

NF = 5, AL = 0.500, BE = 0.000, OGAT = 1.56787-002

TTPP = 90.680, TCRT = 190.555, DTRP = 28.147, DCRT = 10.200

|             |             |            |             |
|-------------|-------------|------------|-------------|
| -0.15965159 | -0.56695380 | 1.02422995 | -0.58857933 |
| 0.29428355  | 0.00000000  | 0.00000000 | 0.00000000  |
| 0.00000000  | 0.00000000  | 0.00000000 | 0.00000000  |

| MOL/L       | CALC        | PCNT  | T,K     | CALC    | PCNT  | DTS/00    |
|-------------|-------------|-------|---------|---------|-------|-----------|
| 1.56786-002 | 1.56786-002 | 0.00  | 90.680  | 90.680  | 0.00  | 5.391+002 |
| 1.62791-002 | 1.62630-002 | 0.02  | 92.000  | 91.938  | -0.00 | 4.775+002 |
| 2.28579-002 | 2.28668-002 | 0.04  | 94.000  | 93.936  | -0.00 | 4.005+002 |
| 2.82943-002 | 2.83065-002 | 0.04  | 96.000  | 95.935  | -0.00 | 3.390+002 |
| 3.46926-002 | 3.47064-002 | 0.04  | 98.000  | 97.936  | -0.00 | 2.893+002 |
| 4.21625-002 | 4.21756-002 | 0.03  | 100.000 | 99.937  | -0.00 | 2.488+002 |
| 5.08186-002 | 5.08288-002 | 0.02  | 102.000 | 101.938 | -0.00 | 2.154+002 |
| 6.07803-002 | 6.07855-002 | 0.01  | 104.000 | 103.939 | -0.00 | 1.878+002 |
| 7.21719-002 | 7.21702-002 | -0.00 | 106.000 | 106.010 | 0.06  | 1.647+002 |
| 8.51224-002 | 8.51123-002 | -0.01 | 108.000 | 108.001 | 0.00  | 1.453+002 |
| 9.97658-002 | 9.97466-002 | -0.02 | 110.000 | 110.002 | 0.00  | 1.288+002 |
| 1.16241-001 | 1.16213-001 | -0.02 | 112.000 | 112.003 | 0.00  | 1.147+002 |
| 1.34692-001 | 1.34659-001 | -0.03 | 114.000 | 114.004 | 0.00  | 1.026+002 |
| 1.55269-001 | 1.55226-001 | -0.03 | 116.000 | 116.014 | 0.00  | 9.221+001 |
| 1.78128-001 | 1.78080-001 | -0.03 | 118.000 | 118.004 | 0.00  | 8.314+001 |
| 2.03431-001 | 2.03383-001 | -0.02 | 120.000 | 120.014 | 0.00  | 7.522+001 |
| 2.31346-001 | 2.31304-001 | -0.02 | 122.000 | 122.003 | 0.00  | 6.827+001 |
| 2.62056-001 | 2.62022-001 | -0.01 | 124.000 | 124.012 | 0.00  | 6.215+001 |
| 2.95748-001 | 2.95725-001 | -0.01 | 126.000 | 126.001 | 0.00  | 5.672+001 |
| 3.32616-001 | 3.32611-001 | -0.00 | 128.000 | 128.000 | 0.00  | 5.189+001 |
| 3.72870-001 | 3.72889-001 | 0.01  | 130.000 | 129.939 | -0.00 | 4.757+001 |
| 4.16733-001 | 4.16780-001 | 0.01  | 132.000 | 131.938 | -0.00 | 4.370+001 |
| 4.64444-001 | 4.64526-001 | 0.02  | 134.000 | 133.937 | -0.00 | 4.021+001 |
| 5.16255-001 | 5.16362-001 | 0.02  | 136.000 | 135.936 | -0.00 | 3.706+001 |
| 5.72441-001 | 5.72579-001 | 0.02  | 138.000 | 137.935 | -0.00 | 3.420+001 |
| 6.33297-001 | 6.33462-001 | 0.03  | 140.000 | 139.935 | -0.00 | 3.159+001 |
| 6.99144-001 | 6.99331-001 | 0.03  | 142.000 | 141.935 | -0.00 | 2.921+001 |
| 7.70334-001 | 7.70534-001 | 0.03  | 144.000 | 143.935 | -0.00 | 2.704+001 |
| 8.47251-001 | 8.47451-001 | 0.02  | 146.000 | 145.935 | -0.00 | 2.503+001 |
| 9.30320-001 | 9.30504-001 | 0.02  | 148.000 | 147.936 | -0.00 | 2.319+001 |
| 1.02001+000 | 1.02016+000 | 0.01  | 150.000 | 149.937 | -0.00 | 2.148+001 |
| 1.11685+000 | 1.11694+000 | 0.01  | 152.000 | 151.938 | -0.00 | 1.989+001 |
| 1.22143+000 | 1.22144+000 | 0.00  | 154.000 | 154.000 | -0.00 | 1.842+001 |
| 1.33441+000 | 1.33433+000 | -0.01 | 156.000 | 156.001 | 0.00  | 1.705+001 |
| 1.45656+000 | 1.45636+000 | -0.01 | 158.000 | 158.003 | 0.00  | 1.576+001 |
| 1.58877+000 | 1.58843+000 | -0.02 | 160.000 | 160.005 | 0.00  | 1.455+001 |
| 1.73204+000 | 1.73156+000 | -0.03 | 162.000 | 162.007 | 0.00  | 1.341+001 |
| 1.83759+000 | 1.83697+000 | -0.03 | 164.000 | 164.008 | 0.00  | 1.234+001 |
| 2.05685+000 | 2.05610+000 | -0.04 | 166.000 | 166.008 | 0.01  | 1.132+001 |
| 2.24155+000 | 2.24073+000 | -0.04 | 168.000 | 168.008 | 0.01  | 1.036+001 |
| 2.44331+000 | 2.44300+000 | -0.03 | 170.000 | 170.008 | 0.00  | 9.433+000 |
| 2.66631+000 | 2.66564+000 | -0.03 | 172.000 | 172.006 | 0.00  | 8.548+000 |
| 2.91249+000 | 2.91214+000 | -0.01 | 174.000 | 174.003 | 0.00  | 7.696+000 |
| 3.18671+000 | 3.18711+000 | 0.01  | 176.000 | 175.939 | -0.00 | 6.871+000 |
| 3.49581+000 | 3.49685+000 | 0.03  | 178.000 | 177.934 | -0.00 | 6.066+000 |
| 3.84823+000 | 3.85034+000 | 0.06  | 180.000 | 179.939 | -0.01 | 5.275+000 |
| 4.25806+000 | 4.26143+000 | 0.08  | 182.000 | 181.935 | -0.01 | 4.488+000 |
| 4.74367+000 | 4.75265+000 | 0.08  | 184.000 | 183.935 | -0.01 | 3.690+000 |
| 5.36526+000 | 5.36679+000 | 0.03  | 186.000 | 185.936 | -0.00 | 2.858+000 |
| 6.22000+000 | 6.20573+000 | -0.23 | 188.000 | 188.028 | 0.01  | 1.935+000 |

NP = 50, DPMSPCT = 0.043, TSPNSPCT = 0.004 M-7



Table 6. Methane Saturated Liquid Temperatures

NF = 5, AL = 0.000, BE = 0.333, DGAT = 1.56787-002

TTRP = 90.680, TCRT = 190.555, DTRP = 28.147, DCRT = 10.200

| 8.53377917<br>0.20671342 |             | -7.05254599<br>0.00000000 |         | 4.16102443<br>0.00000000 |       | -1.36319291<br>0.00000000 |  |
|--------------------------|-------------|---------------------------|---------|--------------------------|-------|---------------------------|--|
| MOL/L                    | CALC        | PCNT                      | T,K     | CALC                     | PCNT  | DTS/DD                    |  |
| 2.81470+001              | 2.81470+001 | 0.00                      | 90.680  | 90.630                   | 0.00  | -1.208+001                |  |
| 2.80378+001              | 2.80375+001 | -0.00                     | 92.000  | 91.936                   | -0.00 | -1.203+001                |  |
| 2.78714+001              | 2.78706+001 | -0.00                     | 94.000  | 93.931                   | -0.01 | -1.194+001                |  |
| 2.77036+001              | 2.77026+001 | -0.00                     | 96.000  | 95.936                   | -0.01 | -1.186+001                |  |
| 2.75344+001              | 2.75332+001 | -0.00                     | 96.000  | 97.936                   | -0.01 | -1.176+001                |  |
| 2.73638+001              | 2.73625+001 | -0.00                     | 100.000 | 99.936                   | -0.01 | -1.167+001                |  |
| 2.71916+001              | 2.71904+001 | -0.00                     | 102.000 | 101.936                  | -0.01 | -1.157+001                |  |
| 2.70179+001              | 2.70167+001 | -0.00                     | 104.000 | 103.937                  | -0.01 | -1.147+001                |  |
| 2.68425+001              | 2.68415+001 | -0.00                     | 106.000 | 105.938                  | -0.01 | -1.136+001                |  |
| 2.66654+001              | 2.66645+001 | -0.00                     | 108.000 | 107.930                  | -0.01 | -1.125+001                |  |
| 2.64865+001              | 2.64857+001 | -0.00                     | 110.000 | 109.932                  | -0.01 | -1.113+001                |  |
| 2.63056+001              | 2.63051+001 | -0.00                     | 112.000 | 111.934                  | -0.01 | -1.101+001                |  |
| 2.61228+001              | 2.61224+001 | -0.00                     | 114.000 | 113.936                  | -0.00 | -1.089+001                |  |
| 2.59379+001              | 2.59377+001 | -0.00                     | 116.000 | 115.938                  | -0.00 | -1.076+001                |  |
| 2.57507+001              | 2.57507+001 | 0.00                      | 118.000 | 118.000                  | 0.00  | -1.063+001                |  |
| 2.55612+001              | 2.55615+001 | 0.00                      | 120.000 | 120.002                  | 0.00  | -1.050+001                |  |
| 2.53693+001              | 2.53697+001 | 0.00                      | 122.000 | 122.004                  | 0.00  | -1.036+001                |  |
| 2.51749+001              | 2.51754+001 | 0.00                      | 124.000 | 124.006                  | 0.00  | -1.022+001                |  |
| 2.49777+001              | 2.49784+001 | 0.00                      | 126.000 | 126.007                  | 0.01  | -1.008+001                |  |
| 2.47776+001              | 2.47784+001 | 0.00                      | 128.000 | 128.008                  | 0.01  | -9.928+000                |  |
| 2.45745+001              | 2.45754+001 | 0.00                      | 130.000 | 130.009                  | 0.01  | -9.775+000                |  |
| 2.43682+001              | 2.43692+001 | 0.00                      | 132.000 | 132.009                  | 0.01  | -9.618+000                |  |
| 2.41595+001              | 2.41595+001 | 0.00                      | 134.000 | 134.009                  | 0.01  | -9.457+000                |  |
| 2.39452+001              | 2.39462+001 | 0.00                      | 136.000 | 136.009                  | 0.01  | -9.292+000                |  |
| 2.37280+001              | 2.37290+001 | 0.00                      | 138.000 | 138.009                  | 0.01  | -9.122+000                |  |
| 2.35067+001              | 2.35076+001 | 0.00                      | 140.000 | 140.008                  | 0.01  | -8.948+000                |  |
| 2.32810+001              | 2.32816+001 | 0.00                      | 142.000 | 142.007                  | 0.01  | -8.768+000                |  |
| 2.30506+001              | 2.30513+001 | 0.00                      | 144.000 | 144.006                  | 0.00  | -8.584+000                |  |
| 2.28152+001              | 2.28158+001 | 0.00                      | 146.000 | 146.005                  | 0.00  | -8.395+000                |  |
| 2.25744+001              | 2.25748+001 | 0.00                      | 148.000 | 148.003                  | 0.00  | -8.200+000                |  |
| 2.23276+001              | 2.23278+001 | 0.00                      | 150.000 | 150.002                  | 0.00  | -7.999+000                |  |
| 2.20746+001              | 2.20745+001 | -0.00                     | 152.000 | 152.000                  | -0.00 | -7.793+000                |  |
| 2.18146+001              | 2.18143+001 | -0.00                     | 154.000 | 153.938                  | -0.00 | -7.579+000                |  |
| 2.15471+001              | 2.15466+001 | -0.00                     | 156.000 | 155.936                  | -0.00 | -7.359+000                |  |
| 2.12713+001              | 2.12705+001 | -0.00                     | 158.000 | 157.935                  | -0.00 | -7.132+000                |  |
| 2.09863+001              | 2.09853+001 | -0.00                     | 160.000 | 159.933                  | -0.00 | -6.896+000                |  |
| 2.06912+001              | 2.06901+001 | -0.01                     | 162.000 | 161.932                  | -0.00 | -6.652+000                |  |
| 2.03849+001              | 2.03835+001 | -0.01                     | 164.000 | 163.931                  | -0.01 | -6.399+000                |  |
| 2.00658+001              | 2.00643+001 | -0.01                     | 166.000 | 165.931                  | -0.01 | -6.135+000                |  |
| 1.97322+001              | 1.97307+001 | -0.01                     | 168.000 | 167.932                  | -0.00 | -5.859+000                |  |
| 1.93820+001              | 1.93807+001 | -0.01                     | 170.000 | 169.933                  | -0.00 | -5.570+000                |  |
| 1.90125+001              | 1.90114+001 | -0.01                     | 172.000 | 171.934                  | -0.00 | -5.265+000                |  |
| 1.86201+001              | 1.86195+001 | -0.00                     | 174.000 | 173.937                  | -0.00 | -4.943+000                |  |
| 1.82004+001              | 1.82004+001 | 0.00                      | 176.000 | 176.000                  | -0.00 | -4.600+000                |  |
| 1.77467+001              | 1.77475+001 | 0.00                      | 178.000 | 178.003                  | 0.00  | -4.232+000                |  |
| 1.72499+001              | 1.72516+001 | 0.01                      | 180.000 | 180.006                  | 0.00  | -3.833+000                |  |
| 1.66958+001              | 1.66963+001 | 0.01                      | 182.000 | 182.008                  | 0.00  | -3.394+000                |  |
| 1.60606+001              | 1.60632+001 | 0.02                      | 184.000 | 184.008                  | 0.00  | -2.903+000                |  |
| 1.52986+001              | 1.52997+001 | 0.01                      | 186.000 | 186.003                  | 0.00  | -2.338+000                |  |
| 1.42978+001              | 1.42937+001 | -0.03                     | 188.000 | 187.933                  | -0.00 | -1.652+000                |  |
| 1.25270+001              | 1.25276+001 | 0.00                      | 190.000 | 190.000                  | 0.00  | -6.700-001                |  |

NP = 51, DNRMSPT = 0.006, TSRMSPT = 0.006

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SUBJECT Liquid-Vapor Saturation (Orthobaric) Temperatures  
of Ethane and Methane

NAME R. D. Goodwin

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## Appendix I. The Computer Programs

## PROGRAM TSATFIT

```

C DESCRIBE ETHANE SATN. TEMPS., TSAT(DEN).
C DEFINE R=D/DTRP, S=D/DCRT, ST=DTRP/DCRT, AND -
C YY(TSAT) = (TCRT/T-1)/(TCRT/TTRP-1), AND -
C
COMMON NG,AL,BE,TTRP,TCRT, DGAT,DTRP,DCRT, DTSR, A(15),B(15)
COMMON/999/NP,NF,H(15),Y(200),G(200,15)
DIMENSION T(99),DEN(99),YY(99),F(15)
DIMENSION UL(99)
2 FORMAT(1H1 30X *ETHANE SATURATION TEMPERATURES* //
1 16X4HNF =I3, 6H, AL =F7.3, 6H, BE =F7.3, 8H, DGAT =E13.5//
1 16X 6HTTRP =F7.3, 8H, TCRT =F8.3, 8H, DTRP =F7.3,
2 8H, DCRT =F6.3// 3(12X 4F16.8/ ) /
315X5HMOL/L 11X4HCALC 5X4HPCNT 8X3HT,K 6X4HCALC 5X4HPCNT6X6HOTS/DD)
3 FORMAT(1H1 14X 5HMOL/L 11X4HCALC 5X4HPCNT
3 8X3HT,K 6X4HCALC 5X4HPCNT 6X6HOTS/DD )
4 FORMAT(5X 2E15.5, F9.2, F11.3, F10.3, F9.2, E12.3)
5 FORMAT(13X 2HNF 13X2HAL 13X2HBF 8X2HSS)
6 FORMAT(10X I5, 2E15.5, F10.3)
9 FORMAT(1HC 6X 4HNP =I3, 12H, DNRMSPT =F6.3, 12H, TSRMSPT =F6.3)
11 TTRP=89.899 $ TCRT=325.33 $ YN = TCRT/TTRP-1
12 DTRP=21.68 $ DCRT=6.87 $ DGAT=1.35114E-6
13 ST=DGAT/DCRT $ VT=1/(1-ST) $ QT=CUBERTF(ST)
C
C SATD. VAPOE TEMPS. CONSTRAINED AT T.P. BY SUBTRACTION -
C EQUATION, YY = U(S)*(1+W(S)), U = EXP(AL*(VT-V)),
C V = 1/ABS(S-1), Q = S**(1/3), AND -
C W = A1*LN(S/ST) + A2*(Q-QT) + A3*(Q2-QT2) + . . .
C GENERATE THE SATD. VAPOR DATA.
25 DO 29 J=1,44 $ IF(J-1) 27,26
26 T(J) = TTRP $ GO TO 28
27 T(J) = 80 + 5*J
28 DEN(J) = DENGASF(T(J))
29 YY(J) = (TCRT/T(J)-1)/YN $ NP = 44
C PRINT FOR NF, GET AL BY TRIAL.
30 AL = 1.50
31 DO 69 NF=4,10 $ NG = NF $ SSK = 1.0E+100
32 DO 40 J=1,NP $ S=DEN(J)/DCRT $ Q=CUBERTF(S) $ V=1/(1-S)
33 U = EXP(AL*(VT-V)) $ G(J,1) = U*LOGF(S/ST)
35 DO 36 K=2,NF $ N = K-1
36 G(J,K) = U*(Q**N - QT**N)
40 Y(J) = YY(J) - U
49 CALL EGENFT $ DO 50 K=1,NF
50 A(K) = H(K) $ SD = SS = 0
51 DO 52 J=1,NP $ TC = TSATF(DEN(J))
52 SS = SS + (TC/T(J)-1)**2 $ SS = 100*SQRTF(SS/NP)
53 IF(SS.LT.SSK) 54,56
54 SSK=SS $ NGK=NG $ ALK=AL $ BEK=BE $ DO 55 K=1,NF
55 F(K) = I(K)
56 CONTINUE
57 CONTINUE $ NG=NGK $ AL=ALK $ BE=BEK $ DO 58 K=1,NF
58 A(K) = F(K) $ SS = SD = 0

```



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SUBJECT

Liquid-Vapor Saturation (Orthobaric) Temperatures of  
Ethane and Methane

NAME

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DATE

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## Appendix I. (continued)

## C PRINT CONSTANTS AND DEVIATIONS.

60 PRINT 2, NG, AL, BE, DGAT, TTRP, TCRT, DTRP, DCRT, (A(K), K=1, 12)

61 DO 67 J=1, NP \$ D=DEN(J) \$ X=T(J) \$ DC=FINDSATF(0, X)

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62 DPCT = 100\*(DC/D-1) \$ SD = SD + DPCT\*DPCT

64 TC = TSATF(D) \$ DTSDD = DTSOR/DTRP

65 TPCT = 100\*(TC/X-1) \$ SS = SS + TPCT\*TPCT

67 PRINT 4, D, DC, DPCT, X, TC, TPCT, DTSDD

68 SD=SQRTF(SD/NP) \$ SS=SQRTF(SS/NP) \$ PRINT 9, NP, SD, SS

69 CONTINUE \$ AL = 0

C

C SATD. LIQUID TEMPS. CONSTRAINED AT THE T.P. BY SUBTRACTION, -  
 C EQN.,  $\ln(YY) = W(S)$ , WHERE  $X = \text{ABS}(S-1)$ ,  $XT = \text{ABS}(ST-1)$ , AND -  
 C  $W(S) = BE*(1/XT-1/X) + B1*(X-XT) + B2*(X^2-XT^2) + \dots$

C GENERATE LIQUID DATA.

70 DO 74 J=1, 44 \$ IF(J-1) 72, 71

71 T(J) = TTRP \$ GO TO 73

72 T(J) = 80 + 5\*J

73 DEN(J) = DENLIQF(T(J))

74 YY(J) = LOGF((TCRT/T(J)-1)/YN)

75 NP = 44 \$ NG = NF = 5 \$ XT = DTRP/DCRT - 1

C SET UP FIXED LEAST SQUARES FUNCTIONS.

80 DO 85 J=1, NP \$ S = DEN(J)/DCRT \$ X = ABSF(S-1)

81 UL(J) = 1/XT - 1/X \$ DO 82 K=1, NF \$ N = K

82 G(J, K) = X\*\*N - XT\*\*N

85 CONTINUE

C FIND NF, BE BY TRIAL.

90 BE = 1.0/3.0 \$ DO 91 J=1, NP

91 Y(J) = YY(J) - BE\*UL(J) \$ CALL EGENFT \$ DO 92 K=1, NF

92 B(K) = H(K) \$ SD = SS = 0

C PRINT LIQUID DEVIATIONS.

100 PRINT 2, NG, AL, BE, DGAT, TTRP, TCRT, DTRP, DCRT, (B(K), K=1, 12)

101 DO 105 J=1, NP \$ D=DEN(J) \$ X=T(J) \$ DC = FINDSATF(1, X)

102 DPCT = 100\*(DC/D-1) \$ SD = SD + DPCT\*\*2

103 TC = TSATF(D) \$ DTSDD = DTSOR/DTRP

104 TPCT = 100\*(TC/X-1) \$ SS = SS + TPCT\*\*2

105 PRINT 4, D, DC, DPCT, X, TC, TPCT, DTSDD

106 SD = SQRTF(SD/NP) \$ SS = SQRTF(SS/NP)

107 PRINT 9, NP, SD, SS

110 CONTINUE

999 STOP \$ END

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## Appendix I. (continued)

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## FUNCTION TSATF(DEN)

COMMON NG,AL,BE,TTRP,TCRT, DGAT,DTRP,DCRT, DTSOR, A(15),B(15)

1 R=DEN/DTRP \$ S=DEN/DCRT \$ QS = S-1 \$ DSDR=DTRP/DCRT \$ IF(QS) 2,30

2 X = ABSF(QS) \$ X1 = DSR\*OS/X \$ YN = TCRT/TTRP - 1

3 V = 1/X \$ V1 = -DSR/QS/X \$ IF(QS) 4,30,15

C CATD. VAPOR TEMPS. CONSTRAINED AT T.P. BY SUBTRACTION -

C EQUATION. YY = U(S)\*(1+W(S)), U = EXP(AL\*(VT-V)),

C V = 1/ABS(S-1), Q = S\*\*(1/3), AND -

C W = A1\*LN(S/ST) + A2\*(Q-QT) + A3\*(Q2-QT2) + . . .

4 ST=DGAT/DCRT \$ VT=1/(1-ST) \$ QT=CUBERTF(ST)

5 U = EXPF(AL\*(VT-V)) \$ U1 = -AL\*V1\*U

6 Q = CUBERTF(S) \$ Q1 = C\*DSOR/3/S

7 W = 1 + A(1)\*LOGF(S/ST) \$ W1 = A(1)\*DSOR/S

8 DO 10 K=2,NG \$ N = K-1

9 W = W + A(K)\*(Q\*\*N - QT\*\*N)

10 W1 = W1 + N\*A(K)\*Q1\*Q\*\*(N-1)

12 F = U\*W \$ F1 = U\*W1 + U1\*W \$ Q = 1 + YN\*F

14 TSATF = TCRT/Q \$ DTSOR = -YN\*F1\*TSATF/Q \$ RETURN

C SATD. LIQUID TEMPS. CONSTRAINED AT THE T.P. BY SUBTRACTION, -

C EQN., LN(YY) = W(S), WHERE X=ABS(S-1), XT=ABS(ST-1), AND -

C W(S) = BE\*(1/XT-1/X) + B1\*(X-XT) + B2\*(X2-XT2) + . . .

15 XT = DSR-1 \$ W = BE\*(1/XT-V) \$ W1 = -BE\*V1

17 DO 19 K=1,NG \$ N = K

18 W = W + B(K)\*(X\*\*N - XT\*\*N)

19 W1 = W1 + B(K)\*N\*X1\*X\*\*(N-1)

20 F = EXPF(W) \$ F1 = W1\*F \$ Q = 1 + YN\*F

22 TSATF = TCRT/Q \$ DTSOR = -YN\*F1\*TSATF/Q \$ RETURN

30 TSATF = TCRT \$ DTSOR = 0 \$ RETURN \$ END

## FUNCTION DENGASF(T)

C ETHANE SATURATED VAPOR DENSITIES, MOL/L.

C Y = A1 + A2\*Q2 + A3\*Q3 + . . . , NF = AL, YN = LN(DCRT/DTRP),

C U = Z + (ZE-Z)\*Y, DEN = DCRT\*EXP(-YN\*U).

DIMENSION A(5)

DATA (TTRP=89.899),(TCRT=305.33),(E=0.362)

DATA (DCRT=6.87),(DTRP=1.35114E-6)

DATA(A = 0.19277431, 0.04155009, -0.78922629,

1 0.35766750, 0.12454376)

1 FORMAT(1H0 9X \*DENGASF = 0, T EXCEEDS TCRT. \* / )

2 IF(TCRT-T) 3,4,5

3 PRINT 1 \$ STOP

4 DENGASF = DCRT \$ DSDT = D2SDT2 = 0 \$ RETURN

5 ZN=TCRT/TTRP-1 \$ YN=LOGF(DCRT/DTRP) \$ Z=(TCRT/T-1)/ZN

6 DZDT = -TCRT/ZN/1/T \$ ZE = Z\*\*E \$ ZE1 = E\*ZE/Z

8 X = ZE-Z \$ X1 = ZE1-1 \$ Q = CUBERTF(Z) \$ Q1 = Q/3/Z

10 Y = A(1) \$ Y1 = 0 \$ DO 13 K=2,5

11 Y = Y + A(K)\*Q\*\*K

12 Y1 = Y1 + K\*A(K)\*Q\*\*(K-1)

13 CONTINUE \$ Y1 = Y1\*Q1

15 U = Z + Y\*Y \$ UA = 1 + X\*Y1 + X1\*Y \$ U1 = UA\*DZDT

16 XP = EXPF(-YN\*U) \$ DENGASF = F = DCRT\*XP

17 DSDT = -YN\*U1\*F \$ RETURN \$ END

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## Appendix I. (continued)

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```

FUNCTION FINDSATF(M,T)
C   THIS FINDSATF ADJUSTED FOR ETHANE.
C   ITERATE DEN TO MINIMIZE (T-TS) VIA TSATF(DEN).
C   1 = 0 FOR VAPOR, M = 1 FOR LIQUID.
COMMON NG,AL,BE,TTRP,TCRT, DGAT,DTRP,DCRT, DTSOR, A(15),B(15)
DATA (DGT=1.0E-6),(DLT=23.0)
1  FORMAT(1H0 9X *FINDSATF = 0, FAILS TO CONVERGE.* / )
2  FORMAT(1H0 9X *FINDSATF = 0, T EXCEEDS TCRT.* / )
3  IF(T-TCRT) 4,22,23
4  IF(M.EQ.0) 5,6
5  D = DENGASF(T) $ GO TO 7
6  D = DENLIQF(T)
7  DO 20 J=1,50 $ DT=T-TSATF(D) $ IF(ABSF(DT/T)-1.0E-6) 21,21,8
8  DTDD = DTSOR/DTRP $ IF(DTDD.EQ.0.0) 22,9
9  DD = DT/DTDD $ IF(ABSF(DT/DD)-1.0E-6) 21,21,10
10 D = D + DD $ IF(M.EQ.0) 11,15
11 IF(D.GT.DGT) 13,12
12 D = DGT $ GO TO 20
13 IF(D.LT.DCRT) 25,14
14 D = DCRT - 0.02 $ GO TO 20
15 IF(D.GT.DLT) 16,17
16 D = DLT $ GO TO 20
17 IF(D.GT.DCRT) 20,18
18 D = DCRT + 0.02
20 CONTINUE $ FINDSATF = 1 $ PRINT 1 $ RETURN
21 FINDSATF = 0 $ RETURN
22 FINDSATF = DCRT $ RETURN
23 FINDSATF = 0 $ PRINT 2 $ RETURN $ END

```

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```

FUNCTION DENLIQF(T)
C   ETHANE SATURATED LIQUID DENSITIES, MOL/L.
C   Y = A1 + A2*Q2 + A3*Q3 + . . . , YN = DTRP-DCRT,
C   DEN = DCRT + YN*(X + (XE-X)*Y).
DATA (TCRT=305.33),(TTRP=89.899),(DCRT=6.87),(DTRP=21.68),(E=0.35)
DATA (A=0.76173503),(B=0.29865351),(C=-0.32762394)
1  FORMAT(1H0 9X *DENLIQF = 0, T EXCEEDS TCRT.* / )
2  IF(TCRT-T) 3,4,5
3  PRINT 1 $ STOP
4  DENLIQF=DCRT $ DRDT=D2FDT2=0 $ RETURN
5  XN=TCRT-TTRP $ YN=DTRP-DCRT $ X=(TCRT-T)/XN $ DXDT=-1/XN
6  XE = X**E $ XE1 = E*XE/X $ W = CUBERTF(X) $ W1 = W/3/X
8  Q = XE-X $ Q1 = XF1-1
9  WW = W*W $ Y = A + B*W + C*X
10 Y1 = 2*B*W + 3*C*WW
11 Y1 = Y1*W1
13 DENLIQF = DCRT + (X + Q*Y)*YN
14 DRDT = (1 + Q*Y1 + Q1*Y)*YN*DXDT $ RETURN $ END

```

## LABORATORY NOTE

SUBJECT Liquid-Vapor Saturation (Orthobaric) Temperatures  
of Ethane and Methane

NAME R.D. Goodwin

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## Appendix I. (continued)

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## FUNCTION DENGASF(T)

```

C METHANE SAT. VAPOR DEN, MOL/L, VIA VAPORFIT, 11/19/73.
C  $Y = A1 + A2*Q2 + A3*Q3 + \dots$ ,  $NF = AL$ ,  $YN = LN(DCRT/DTRP)$ ,
C  $U = Z + (ZE-Z)*Y$ ,  $DEN = DCRT*EXP(-YN*U)$ .
  DIMENSION A(5)
  DATA (TTRP=90.68), (TCRT=190.555), (E=0.388)
  DATA (DCRT=10.2), (DTRP=0.01567865)
  DATA (A = 0.3925579, -0.4976888, 1.3200516,
1 -1.6817790, 0.6848609)
1 FORMAT(1H0 9X *DENGASF = 0, T EXCEEDS TCRT. * / )
2 IF (TCRT-T) 3,4,5
3 PRINT 1 $ STOP
4 DENGASF = DCRT $ DROT = D2ROT2 = 0 $ RETURN
5 ZN=TCRT/TTRP-1 $ YN=LOGF(DCRT/DTRP) $ Z=(TCRT/T-1)/ZN
6 DZDT = -TCRT/ZN/T/T $ ZE = Z**E $ ZE1 = E*ZE/Z
8 X = ZE-Z $ X1 = ZE1-1 $ Q = CUBERTF(Z) $ Q1 = Q/3/Z
10 Y = A(1) $ Y1 = 0 $ DO 13 K=2,5
11 Y = Y + A(K)*Q**K
12 Y1 = Y1 + K*A(K)*Q**(K-1)
13 CONTINUE $ Y1 = Y1*Q1
15 U = Z + X*Y $ UA = 1 + X*Y1 + X1*Y $ U1 = UA*DZDT
16 XP = EXPF(-YN*U) $ DENGASF = F = DCRT*XP
17 DROT = -YN*U1*F $ RETURN $ END

```

## FUNCTION DENLIQF(T)

```

C METHANE SATD. LIQUID DEN, MOL/L, VIA LAB. NOTE 73-5.
C  $Y = A1 + A2*Q2 + A3*Q3 + \dots$ ,  $YN = DTRP-DCRT$ ,
C  $DEN = DCRT + YN*(X + (XE-X)*Y)$ .
  DATA (TTRP=90.68), (TCRT=190.555), (E=0.361)
  DATA (DCRT=10.2), (DTRP=28.147)
  DATA (A=0.83709103), (B=0.08416127), (C=-0.07478575)
1 FORMAT(1H0 9X *DENLIQF = 0, T EXCEEDS TCRT. * / )
2 IF (TCRT-T) 3,4,5
3 PRINT 1 $ STOP
4 DENLIQF=DCRT $ DROT=D2ROT2=0 $ RETURN
5 XN=TCRT-TTRP $ YN=DTRP-DCRT $ X=(TCRT-T)/XN $ DXDT=-1/XN
6 XE = X**E $ XE1 = E*XE/X $ W = CUBERTF(X) $ W1 = W/3/X
8 Q = XE-X $ Q1 = XE1-1
9 WW = W*W $ Y = A + B*WW + C*X
10 Y1 = 2*3*W + 3*C*WW
11 Y1 = Y1*W1
13 DENLIQF = DCRT + (X + Q*Y)*YN
14 DROT = (1 + Q*Y1 + Q1*Y)*YN*DXDT $ RETURN $ END

```





## APPENDIX N

LOW-TEMPERATURE ELASTIC PROPERTIES OF ALUMINUM 5083-0  
AND FOUR FERRITIC NICKEL STEELS<sup>†</sup>

W. F. Weston,\* E. R. Naimon,\* and H. M. Ledbetter

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ABSTRACT

The low-temperature elastic properties have been determined for five commercial alloys that have possible structural applications at cryogenic temperatures. The alloys are 5083-0 aluminum and four ferritic steels: 3.5, 5, 6, and 9 percent nickel. An ultrasonic (10 MHz) pulse-superposition method was used to measure longitudinal and transverse wave velocities. Using the velocities and the mass density as input, the following moduli were calculated: longitudinal modulus, Young's (tensile) modulus, shear (rigidity) modulus, bulk modulus (reciprocal compressibility), and Poisson's ratio. Measurements were made semi-continuously from 300 K to 4 K. The composition dependence of iron-nickel alloys is reviewed comprehensively up to 12 percent nickel. Debye temperatures were calculated from the elastic constants. A discussion is given of the temperature dependences of the elastic constants, differential relationships among the elastic constants, and the possible relationships between elastic and plastic properties.

Key Words: Aluminum alloy; bulk modulus; compressibility; Debye temperature; elastic constant; nickel steels; Poisson's ratio; shear modulus; sound velocity; Young's modulus.

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\* NRC-NBS Postdoctoral Research Associate, 1973-4.

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# LOW-TEMPERATURE ELASTIC PROPERTIES OF ALUMINUM 5083-0 AND FOUR FERRITIC NICKEL STEELS

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## INTRODUCTION

The recent expansion of cryogenic technology to extensive use of liquefied gases has created new materials problems. In particular, detailed knowledge and understanding of the mechanical properties of common metals and alloys are required. The temperature range of interest is from room temperature to near absolute zero. For engineering, the most important mechanical properties in cryogenic applications are strength (sometimes strength-to-density ratio) and toughness (resistance to low-temperature embrittlement). In this paper, the elastic properties of several common alloys are reported between 300 and 4 K. These properties--Young's modulus, shear modulus, etc.--are essential engineering design parameters, are useful parameters in alloy development, are fundamental data for fracture analysis and theories of solid-solution strengthening, figure prominently in dislocation-model descriptions of mechanical properties, and can be related empirically to a variety of phenomena associated with plastic deformation. Gilman<sup>1</sup> has maintained that "the most important mechanical characteristic of a crystal is its elastic modulus." The elastic moduli of polycrystalline aggregates are also paramount.

It is well known<sup>2</sup> that the major contributions of the addition of small amounts of nickel to steel are: (1) hardening of the ferritic alpha phase; (2) retarding the bainite and pearlite transformations; (3) lowering the  $\gamma$ - $\alpha$  transition temperature, which enables nickel steels to be hardened by quenching at lower temperatures; and (4) resistance to embrittlement at low temperatures. Thus, nickel steels are well suited for cryogenic applications.

Three and one-half percent nickel steel is a weldable low-carbon steel

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\* NRC-NBS Postdoctoral Research Associate, 1973-4.

useful at temperatures down to about  $-100^{\circ}\text{C}$ . Its possible applications include the containment at atmospheric pressure of liquid ethylene and other liquefied gases of higher boiling points, such as ethane, acetylene, carbon dioxide, and propane. Five percent nickel steel is useful at temperatures down to about  $-120^{\circ}\text{C}$  in its quenched-and-tempered state and down to lower temperatures in its austenitized, temperized, reversion-annealed state; and nine percent nickel steel is useful down to liquid nitrogen temperatures ( $-196^{\circ}\text{C}$ ). This alloy may contain as much as 15 percent austenite and could be used for the containment of liquefied oxygen, argon, and nitrogen.

Aluminum alloys also are particularly useful for low-temperature applications, since at cryogenic temperatures their strength increases without loss of ductility. In particular, the 5000 series alloys contain magnesium as the major alloying constituent; magnesium is very effective as a hardener. Alloys in this series possess good welding characteristics and good resistance to corrosion in marine atmosphere.

The low-temperature elastic properties are reported here for five commercial alloys that have possible structural applications at cryogenic temperatures. These alloys are 5083 aluminum and four ferritic steels: 3.5, 5, 6, and 9 percent nickel. An ultrasonic (10 MHz) pulse-superposition method was used to measure longitudinal and transverse wave velocities. Using the velocities and the mass density as input, the following moduli were calculated: longitudinal modulus, Young's (tensile) modulus, shear (rigidity) modulus, bulk modulus (reciprocal compressibility), and Poisson's ratio. Measurements were made semi-continuously from 300 K to 4 K.

These data have been compared to previously reported results and used to calculate the elastic Debye temperatures. Also, the elastic moduli have been used to deduce information on some of the plastic properties of the materials.

Most engineering alloys selected for cryogenic use have close-packed crystal structures; these include austenitic steels and alloys of aluminum, copper, nickel, and titanium. Commercial purity body-centered cubic alloys

tend to have high ductile-to-brittle transition temperatures, that is, a high notch sensitivity. The nickel steels reported on here are a notable exception to the general exclusion of body-centered alloys from cryogenic structures.

## EXPERIMENTAL

The alloy specimens were obtained from commercial sources in the form of plates. The nickel steels were used as-received (quenched and tempered in the cases of the 3.5 and 9.0 percent nickel specimens, and austenitized, temperized, and reversion annealed in the cases of the 5 and 6 percent nickel specimens). The 5083 aluminum was annealed at 413°C for 30 min. at a pressure of  $5 \times 10^{-6}$  torr and cooled in the furnace. Cylindrical specimens 5/8-in. (1.6 - cm) in diameter and 3/8 - in. (1.0 - cm) long were prepared by grinding. Opposite faces were flat and parallel within  $100 \times 10^{-6}$  in. ( $2.5 \mu\text{m}$ ). Chemical compositions (obtained from mill analyses), hardness numbers, and mass densities are given in Table 1. Hardness was determined by standard metallurgical methods. Mass density was determined by Archimedes' method using distilled water as a standard.

Quartz transducers (10 MHz) were bonded to the specimens with phenyl salicylate for room-temperature measurements and with a stopcock grease for lower temperatures. The specimen holder is shown in Fig. 1. The holder was placed in the ullage of a helium dewar and lowered stepwise to achieve cooling. Temperatures were monitored with a chromel-constantan thermocouple contacting the specimen.

Ultrasonic sound-wave velocities, both longitudinal and transverse, were determined by a pulse-superposition technique.<sup>3-5</sup> High-frequency pulses (nominally 10 MHz) were gated from a continuous carrier in such a way that they were all phase coherent. Each pulse, when applied to the quartz transducer, generated an echo train in the specimen. The repetition rate of the pulses was adjusted so that each pulse was superposed on the second echo of each preceding pulse. Thus, the transit time of a sound wave in the specimen is directly related to the repetition rate of the pulses. Denoting the carrier



frequency by  $f$ , the repetition rate is then  $f/n$ , where  $n$  is an integer. Typical values of  $n$ , which are determined from the frequency-divider setting, were 70-200 for these experiments. It follows that the round-trip transit time  $t$  in the specimen is simply

$$t = n/(2f) . \quad (1)$$

Ultrasonic velocities  $v$  are given by

$$v = 2\ell/t, \quad (2)$$

where  $\ell$  is the specimen length. A block diagram of the experimental apparatus is shown in Fig. 2.

In practice the pulse-superposition method proceeded as follows. The carrier frequency  $f$  was adjusted as closely as possible to the resonant frequency of the quartz transducer (nominally 10 MHz). The frequency-divider setting  $n$  was then varied until each pulse was approximately superposed on the second echo from each preceding pulse. The carrier frequency was then readjusted until a maximum constructive interference condition was obtained. A change in the environmental conditions of the specimen caused a change in the transit time, and thus in the interference condition. As the environment changed, superposition was maintained by adjusting the carrier frequency. The divider setting was kept constant for a given experiment. Thus, the experimentally measured quantity was  $\Delta f/f$ . It is easily shown that

$$\Delta t/t = -\Delta f/f, \quad (3)$$

and that

$$\Delta v/v = \Delta f/f + \Delta \ell/\ell. \quad (4)$$

Since an elastic modulus  $C$  is related to the velocity  $v$  and mass density  $\rho$  by

$$C = \rho v^2, \quad (5)$$

it follows that

$$\Delta C/C = \Delta \rho/\rho + 2\Delta v/v. \quad (6)$$

Since  $\Delta\rho/\rho = -3\Delta\ell/\ell$ , one then obtains

$$\Delta C/C = 2\Delta f/f - \Delta\ell/\ell. \quad (7)$$

Changes of elastic moduli due to temperature effects were determined. The measured quantities were thus  $\frac{1}{f} \frac{\Delta f}{\Delta T}$ , where T is absolute temperature. Since the thermal expansion coefficient  $\alpha$  is defined as

$$\alpha = \frac{1}{\ell} \frac{\Delta\ell}{\Delta T}, \quad (8)$$

it follows that

$$\frac{1}{C} \frac{\Delta C}{\Delta T} = 2 \left( \frac{1}{f} \frac{\Delta f}{\Delta T} \right) - \alpha. \quad (9)$$

At room temperature, elastic moduli typically change linearly with temperature. The temperature coefficient  $(1/C) (dC/dT)$  is then significant, since it gives the relative modulus change with temperature. Room-temperature values of the temperature coefficients are reported in this paper.

It is usually found that the thermal-expansion contribution to  $(1/C) (dC/dT)$  is less than 10% of the velocity contribution, that is,  $|\alpha| \leq 2 |(1/f) (df/dT)|$ . Thus, errors in the thermal expansion coefficient will not lead to significant errors in the temperature coefficients of the elastic moduli.

Except for determining room-temperature values of  $(1/C) (dC/dT)$ , effects of thermal expansion are neglected in this paper. Typically an elastic modulus changes by only 5-10% over the temperature range 4-300K, and neglect of thermal expansion leads to an error of at most 0.5% in the low-temperature value of the elastic modulus. Such errors are well within experimental accuracy. Thus, when elastic-moduli — temperature curves were fit to a semi-theoretical function, as discussed below, thermal expansion was neglected.

Relative velocity changes as small as  $10^{-5}$  could be detected; however, absolute errors in the measured moduli are estimated to be about 1-2 percent. Thus, since the individual data points are normalized to the room-temperature value, the overall curve could be shifted by 1 or 2 percent because of systematic error.

## RESULTS

From the longitudinal and transverse ultrasonic velocities,  $v_\ell$  and  $v_t$ , the respective elastic moduli are given by:

$$C_\ell = \rho v_\ell^2, \quad (10)$$

and 
$$C_t = \rho v_t^2, \quad (11)$$

where  $\rho$  is the mass density.

While polycrystalline aggregates (quasi-isotropic solids) have only two independent elastic constants, several constants are commonly used for various applications. The four most common are the bulk modulus  $B$ , Young's modulus  $E$ , the shear modulus  $G$ , and Poisson's ratio  $\nu$ . These constants can be calculated from  $C_\ell$  and  $C_t$  by the relationships

$$E = 3C_t (C_\ell - \frac{4}{3} C_t) / (C_\ell - C_t), \quad (12)$$

$$B = C_\ell - \frac{4}{3} C_t, \quad (13)$$

$$\nu = \frac{1}{2} (C_\ell - 2C_t) / (C_\ell - C_t), \quad (14)$$

and 
$$G = C_t. \quad (15)$$

Rather than calculate the temperature dependence of these four elastic constants point by point from the experimental moduli,  $C_\ell$  and  $C_t$  can be fit to a semi-theoretical relationship suggested by Varshni<sup>6</sup>:

$$C = C^0 - s/(e^{t/T} - 1), \quad (16)$$

where  $C^0$ ,  $s$ , and  $t$  are adjustable parameters and  $T$  is the temperature. The value of  $C$  at  $T = 0$  K is  $C^0$ , and  $-s/t$  is the high-temperature limit of  $dC/dT$ . By invoking an Einstein oscillator model of solids, it can be shown (in the absence of electronic effects) that  $t$  is the Einstein characteristic temperature. The elastic constants can then be calculated from the moduli using Eqs. 12-15.

### A. 5083 Aluminum

Longitudinal ( $C_\ell$ ) and transverse ( $C_t = G$ ) moduli are shown in Figs. 3 and 4. Room-temperature values of the elastic constants are given in Table 2 and room-temperature values of the temperature coefficients of the elastic constants are given in Table 3. Values of commercially pure aluminum (1100 aluminum) are included for comparison.

Curves in Figs. 3 and 4 are plots of Eq. 16 determined by an unweighted least-squares fit of the data. Average percentage differences between measured and curve values are 0.03% and 0.10% for the longitudinal and transverse moduli, respectively. Parameters  $C_0$ ,  $s$ , and  $t$  are given in Table 4.

The elastic constants were calculated from the moduli shown in Figs. 3 and 4 by Eqs. 12-14. The constants  $E$ ,  $B$ , and  $\nu$  are shown in Figs. 5-7.

#### B. Ferritic Nickel Steels

Longitudinal and transverse moduli for the four nickel steels are shown in Figs. 8 and 9. Two of the nickel steels, 5 and 6 percent nickel, exhibit maxima at low temperatures. These maxima may be caused by magnetic transitions. The occurrence of these maxima, however, necessitated fitting the low-temperature data to a different function. The Varshni function (Eq. 16) was fit to the data from room temperature to the maximum. The dashed curve represents a continuation of the Varshni function. From 0 K to the maximum, a polynomial of the form

$$C = C_0 + A\tau^2 + B\tau^3 + D\tau^4 \quad (17)$$

was used to fit the data, where  $C_0$ ,  $A$ ,  $B$ , and  $D$  are adjustable parameters and  $\tau = T/T_{\max}$ , where  $T$  is the temperature and  $T_{\max}$  is the temperature at which the maximum occurs. Since this function has no physical significance, the parameters are not reported. However, the function does satisfy the requirement that the slope go to zero as  $T$  approaches zero. Also it was required that the slope go to zero as  $T$  approaches  $T_{\max}$ .

Room-temperature values of the elastic constants are given in Table 2, and room-temperature values of the temperature coefficients of the elastic constants are given in Table 3. Average percentage differences between measured and curve values vary between 0.01% and 0.04% for the longitudinal moduli and 0.02% to 0.04% for the transverse moduli. The constants  $E$ ,  $B$ , and  $\nu$  are shown in Figs. 10-12.

### C. Elastic Debye Temperatures

It is of interest to calculate the elastic Debye temperature  $\theta$  for the alloys. This fundamental parameter is important in the lattice properties of solids and is related to the elastic wave velocities by <sup>7</sup>

$$\theta = K \langle v \rangle, \quad (18)$$

where

$$K = \frac{h}{k} \left( \frac{3N\rho}{4\pi A} \right)^{1/3} \quad (19)$$

Here  $h$  is Planck's constant,  $k$  is Boltzmann's constant,  $N$  is Avogadro's constant,  $\rho$  is the mass density, and  $A$  is the atomic weight. The average velocity is given by

$$v = \left( \frac{v_l^{-3} + 2v_t^{-3}}{3} \right)^{-1/3} \quad (20)$$

The Debye temperatures for the nickel steels and 5083 aluminum at  $T = 0$  K are given in Table 5. The Debye temperatures of iron and commercially pure aluminum are included for comparison.

### DISCUSSION

The elastic properties of 5083 aluminum behave regularly with respect to temperature. The elastic moduli ( $C_l$ ,  $C_t = G, B, E$ ) decrease with increasing temperature, show a relative flatness at low temperatures, achieve zero slope at  $T = 0$  K, and approach linear behavior at high temperatures. Poisson's ratio also behaves regularly, having a positive temperature coefficient.

As mentioned earlier, however, the moduli of two of the nickel steels (5 and 6 percent nickel) behave anomalously at low temperatures. The moduli first increase with increasing temperature, then decrease approaching linear behavior. Both  $C_l$  and  $C_t$  exhibit a maximum at approximately the same temperature. The 6 percent alloy was checked on both heating and cooling, and no hysteresis seemed to be associated with the anomaly. This behavior is similar to that of some stainless steels,<sup>8</sup> which undergo paramagnetic to antiferromagnetic transitions at low temperatures. Possibly, the anomalies are caused by some magnetic transition.



It is emphasized that the data reported here are dynamic (adiabatic) rather than static (isothermal) and apply to rapid, rather than slow loading. In most cases the differences between adiabatic and isothermal elastic constants are small, less than one percent. Conversion formulas are given by Landau and Lifshitz,<sup>9</sup> for example.

Of the many possible engineering elastic constants (five -  $C_\ell$ ,  $E$ ,  $G$ ,  $B$ , and  $\nu$  - are discussed herein), only two are independent. Both isotropic and quasi-isotropic solids are characterized elastically by two constants. Thus,  $n-2$  independent relationships must exist among  $n$  variables. By differentiation, several quite useful relationships can be obtained. These include:

$$\frac{dC_\ell}{C_\ell} = \frac{1}{B + \frac{4}{3}G} (dB + \frac{4}{3} dG), \quad (21)$$

$$\frac{dE}{E} = \frac{G}{G + 3B} \cdot \frac{dB}{B} + \frac{3B}{G + 3B} \cdot \frac{dG}{G} \quad (22)$$

$$\frac{dB}{B} = \frac{dE}{E} + \frac{2}{1-2\nu} d\nu, \quad (23)$$

$$\frac{dG}{G} = \frac{dB}{B} - \frac{3}{(1+\nu)(1-2\nu)} d\nu, \quad (24)$$

and

$$\frac{d\nu}{\nu} = \frac{E}{E-2G} \cdot \left( \frac{dE}{E} - \frac{dG}{G} \right) \quad (25)$$

If  $\nu \approx \frac{1}{3}$ , which is a typical value for most metals and alloys, then these equations simplify to

$$\frac{dC}{C}_l \approx \frac{2}{3} \frac{dB}{B} + \frac{1}{3} \frac{dG}{G}, \quad (26)$$

$$\frac{dE}{E} \approx \frac{dB}{9B} + \frac{8}{9} \cdot \frac{dG}{G}, \quad (27)$$

$$\frac{dB}{B} \approx \frac{dE}{E} + 2 \frac{d\nu}{\nu}, \quad (28)$$

$$\frac{dG}{G} \approx \frac{dB}{B} - \frac{9}{4} \cdot \frac{d\nu}{\nu}, \quad (29)$$

and

$$\frac{d\nu}{\nu} \approx 4 \left( \frac{dE}{E} - \frac{dG}{G} \right) \approx \frac{4}{9} \left( \frac{dB}{B} - \frac{dG}{G} \right) \quad (30)$$

These relationships contain some surprising and useful information. For example: Young's modulus is eight times more sensitive to shear than to dilatation; Poisson's ratio depends equally, but oppositely, on shear and dilatation, and only on the B/G ratio; the longitudinal modulus is twice as sensitive to dilatation as to shear, etc.

Furthermore, these relationships can be used to predict a wide variety of effects when only partial information is available. Equations (26)-(30) can be expressed generally as

$$\frac{dX}{X} \approx a \frac{dY}{Y} + b \frac{dZ}{Z}, \quad (31)$$

where X, Y, and Z are elastic constants and a and b are numerical coefficients. Much more powerful relationships result by introducing another variable V:

$$\frac{1}{X} \frac{dX}{dV} \approx \frac{a}{Y} \frac{dY}{dV} + \frac{b}{Z} \frac{dZ}{dV}, \quad (32)$$

where V represents any independent variable such as temperature, pressure, or composition. As a useful example, these relationships will now be used to discuss the effects of nickel on the elastic properties of iron.

The existing data<sup>10-28</sup> on the room-temperature elastic constants of nickel-steels are presented in Figs. 13-16. Data for pure iron, obtained by a

Voigt-Reuss-Hill-arithmetic average of single-crystal data<sup>29</sup> are also included. The data were least-squares fitted to a straight line, the slope of which is included in the figures. The data of Speich, Schwoeble, and Leslie was omitted from the least-squares fit for the bulk modulus and Poisson's ratio.

If, in Eq. (32),  $V$  represents composition, the change with composition in one elastic constant can be found from the measured changes with composition in two others. For example, considerably more data exists for Young's modulus and the shear modulus of nickel steels than for Poisson's ratio. Using Eq. (21), however, the compositional dependence of  $\nu$  can be found from  $E$  and  $G$  data:

$$\frac{1}{\nu} \frac{d\nu}{dV} \approx 4 \left( \frac{1}{E} \frac{dE}{dV} - \frac{1}{G} \frac{dG}{dV} \right), \quad (33)$$

or

$$\frac{d\nu}{dV} \approx \frac{4}{3} \left( \frac{1}{2} \frac{dE}{dV} - .8 \frac{dG}{dV} \right), \quad (34)$$

since  $\nu \approx \frac{1}{3}$ ,  $E \approx 2 \times 10^{11} \text{ N/m}^2$  and  $G \approx .8 \times 10^{11} \text{ N/m}^2$  for iron. Using the slopes given in Figs. 13 and 14 as values for  $dE/dV$  and  $dG/dV$ ,  $d\nu/dV \approx 6.7 \times 10^{-4}$ . The slope given in Fig. 16 is  $\sim 7 \times 10^{-4}$ . Similarly, if the  $G$  and  $B$  data are used in Eq. 27 (with  $B \approx 1.6 \times 10^{11} \text{ N/m}^2$ ), then  $dE/dV \approx -2.19 \times 10^9 \text{ N/m}^2$ , in very good agreement with the measured value of  $-2.22 \times 10^9 \text{ N/m}^2$ . In fact, using the  $E$  and  $G$  data to calculate the compositional dependence of  $B$  and  $\nu$  justifies excluding the Speich et al. data from the linear least-squares fit for the compositional dependence of  $B$  and  $\nu$ .

The Debye temperatures of the nickel steels are lower than the Debye temperatures of either iron or nickel<sup>24, 29</sup>. This is expected since the elastic constants, and thus the sound velocities, decrease drastically with the addition of nickel to iron. In fact, the largest known alloying effects on elastic constants may occur for iron-nickel alloys.<sup>28</sup> This effect is not completely understood, but may in part be caused by magnetic interactions.

Finally, the relationship between elastic and plastic properties is discussed briefly, and the possible use of elastic data for predicting plastic properties is indicated. The importance of this is two-fold. First, for cryogenic engineering applications the most important properties of metals are strength and toughness. Second, the possible relationships between elastic and plastic properties seem to be generally unappreciated.

Usually, elastic and plastic behavior are considered separately. For example, in a typical stress-strain experiment the elastic and plastic regions can be separated by an elastic limit, a proportional limit, or sometimes a yield point. While these concepts differ from each other and are not always well-defined and reproducible experimentally, they serve to define a stress level that if exceeded results in permanent, plastic, irreversible mechanical deformation.

The most obvious link between elastic and plastic properties is provided by a dislocation model of microplastic mechanical behavior. All students of dislocation theory know that the mathematical equations describing phenomena such as slip, yielding, bending, cleavage, etc. from a dislocation viewpoint almost always contain elastic constants as material parameters. In an isotropic elasticity model these constants are Young's modulus, the shear modulus, and Poisson's ratio. Isotropy is, of course, an idealization since all real materials are anisotropic in some way.

Despite its potentially high impact, surprisingly little work on elastic-plastic relationships has been published. The advantages that might accrue from such work include: (a) the ability to relate plasticity more intimately to interatomic forces; (b) the possibility of correlating plastic properties with other parameters via the elastic constants — for example atomic number, melting temperature, or Debye theta; and (c) a possibly higher degree of correlation among plastic properties themselves. Some correlations — for example, between Young's modulus and yield stress, or between microhardness and the shear modulus — are already well known.<sup>1</sup>

The most thorough study of the elastic-plastic relationship was made by Pugh.<sup>32</sup> Other studies have been made by Hasselman<sup>33</sup> and by Crutchley and Reid.<sup>34</sup> Pugh made the following suggestions: (1) at temperatures less than one third of its melting point, a material's resistance to plastic deformation

is proportional to  $Gb$ , where  $G$  is the shear modulus, and  $b$  is the magnitude of the Burgers vector; (2) fracture strength is proportional to  $Ba$ , where  $B$  is the bulk modulus, and  $a$  is the lattice parameter; (3) ductility increases with  $B/G$ , the ratio of the bulk modulus to the shear modulus. Since Poisson's ratio  $\nu$  is an increasing monotonic function of  $B/G$ , ductility should also increase with Poisson's ratio; most data support his suggestion -- lead ( $\nu = 0.40$ ), aluminum ( $\nu = 0.37$ ), copper ( $\nu = 0.34$ ), chromium ( $\nu = 0.25$ ), beryllium ( $\nu = 0.04$ ) as examples. Since Poisson's ratio changes only very slowly with alloying, mechanical deformation, etc., it does not provide as sensitive an index of ductility as would be desired. On the other hand, small changes in Poisson's ratio may correspond to large changes in ductility. A possible large influence of  $\nu$  on the plastic anisotropy of b.c.c. metals was discussed by Crutchley, Reid, and Webster.<sup>35</sup> In terms of the iron-nickel alloys reported on here, the following inferences would be drawn from the room-temperature elastic data: (1) the plastic resistance decreases with increasing nickel content; (2) the fracture strength decreases slightly with increasing nickel content; and (3) the ductility, as measured by  $B/G$  increases slightly with increasing nickel content. The experimental study by Jolley<sup>36</sup> contradicts the first two assertions while affirming the third. The poor correlation in this case between elastic and plastic properties suggests either that the particular dislocation models used by Pugh<sup>32</sup> are too simple or that alloying nickel into iron changes somehow the behavior of dislocations in the alloy. For example, atomic ordering could cause localized effects on dislocations that would not be revealed by macroscopic elastic constants.

This leads naturally to another topic, which is especially important in the cryogenic application of iron-nickel alloys -- the ductile - brittle transition. The elastic data in Figs. 8-12 show no irregularities near temperatures where the ductile-brittle transitions occur. This is expected since acoustic waves sample a macroscopic volume of a specimen, and the modulus defect due to dislocations is quite small. Assuming the ductile-brittle transition results from immobilizing dislocations, then measurement of ultrasonic attenuation would be a better approach than measurement of ultrasonic velocities, if in these alloys dislocations contribute significantly to the attenuation.



### Acknowledgment

Specimens of nickel steels were graciously supplied by Armco Steel Corporation and by Nippon Steel Corporation.

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Table 1. Compositions and Properties of Alloys

| Alloy     | Chemical Composition, Mill Analyses (wt. pct.) |     |      |      |      |      |      |     |      |      |      | Hardness<br>(DPH No., 1 kg Load) | Mass Density<br>at 294 K<br>(g/cm <sup>3</sup> ) |
|-----------|------------------------------------------------|-----|------|------|------|------|------|-----|------|------|------|----------------------------------|--------------------------------------------------|
|           | Fe                                             | C   | Mn   | P    | S    | Si   | Ni   | Cr  | Mo   | Al   | N    |                                  |                                                  |
| Fe-3.5 Ni | Bal                                            | .10 | .46  | .015 | .013 | .20  | 3.62 | --  | --   | --   | --   | 174                              | 7.858                                            |
| Fe-5 Ni   | Bal                                            | .13 | .45  | .025 | .025 | .275 | 5.00 | --  | .275 | .085 | .020 | 233                              | 7.821                                            |
| Fe-6 Ni   | Bal                                            | .06 | 1.12 | .005 | .004 | .24  | 5.66 | .63 | .18  | --   | --   | 246                              | 7.821                                            |
| Fe-9 Ni   | Bal                                            | .06 | .56  | .007 | .003 | .27  | 9.25 | --  | --   | --   | --   | 260                              | 7.841                                            |
|           |                                                |     |      |      |      |      |      |     |      |      |      |                                  |                                                  |
|           | Al                                             | Si  | Fe   | Cu   | Mn   | Mg   | Cr   | Zn  | Ti   | V    | Ni   |                                  |                                                  |
| Al 5083   | Bal                                            | .08 | .19  | 04   | .63  | 4.75 | .13  | .04 | .01  | .007 | .003 | 78                               | 2.666                                            |



Table 2. Room Temperature Values of Elastic Constants  
( $10^{11}$  N/m<sup>2</sup> except  $\nu$  (dimensionless))

| Alloy     | E     | G     | B     | $\nu$ |
|-----------|-------|-------|-------|-------|
| Al 5083   | 0.716 | 0.269 | 0.716 | 0.333 |
| Al 1100*  | 0.695 | 0.259 | 0.724 | 0.340 |
| Fe-3.5 Ni | 2.038 | 0.791 | 1.600 | 0.288 |
| Fe-5 Ni   | 1.984 | 0.770 | 1.559 | 0.288 |
| Fe-6 Ni   | 2.024 | 0.790 | 1.543 | 0.281 |
| Fe-9 Ni   | 1.951 | 0.754 | 1.562 | 0.292 |
| Fe **     | 2.05  | 0.81  | 1.664 | 0.282 |

\* Calculated from data taken by the authors.

\*\* Reference 31.

Table 3. Logarithmic Temperature Derivatives of Elastic Constants  
at Room Temperature ( $10^{-4} \text{ K}^{-1}$ )

| Alloy       | $\frac{1}{B} \frac{dB}{dT}$ | $\frac{1}{E} \frac{dE}{dT}$ | $\frac{1}{G} \frac{dG}{dT}$ | $\frac{1}{\nu} \frac{d\nu}{dT}$ |
|-------------|-----------------------------|-----------------------------|-----------------------------|---------------------------------|
| Al 5083     | -2.15                       | -6.29                       | -6.81                       | 2.08                            |
| Al 1100*    | -2.24                       | -5.25                       | -5.60                       | 1.41                            |
| Fe - 3.5 Ni | -1.56                       | -2.82                       | -3.02                       | 0.93                            |
| Fe - 5 Ni   | -1.53                       | -3.32                       | -3.61                       | 1.32                            |
| Fe - 6 Ni   | -1.42                       | -3.21                       | -3.52                       | 1.40                            |
| Fe - 9 Ni   | -1.25                       | -2.77                       | -3.01                       | 1.08                            |
| Fe **       | -0.90                       | -2.11                       | -2.31                       | 0.95                            |

\* Calculated from data taken by the authors.

\*\* Calculated from data in Reference 24 using a Voigt-Reuss-Hill average.

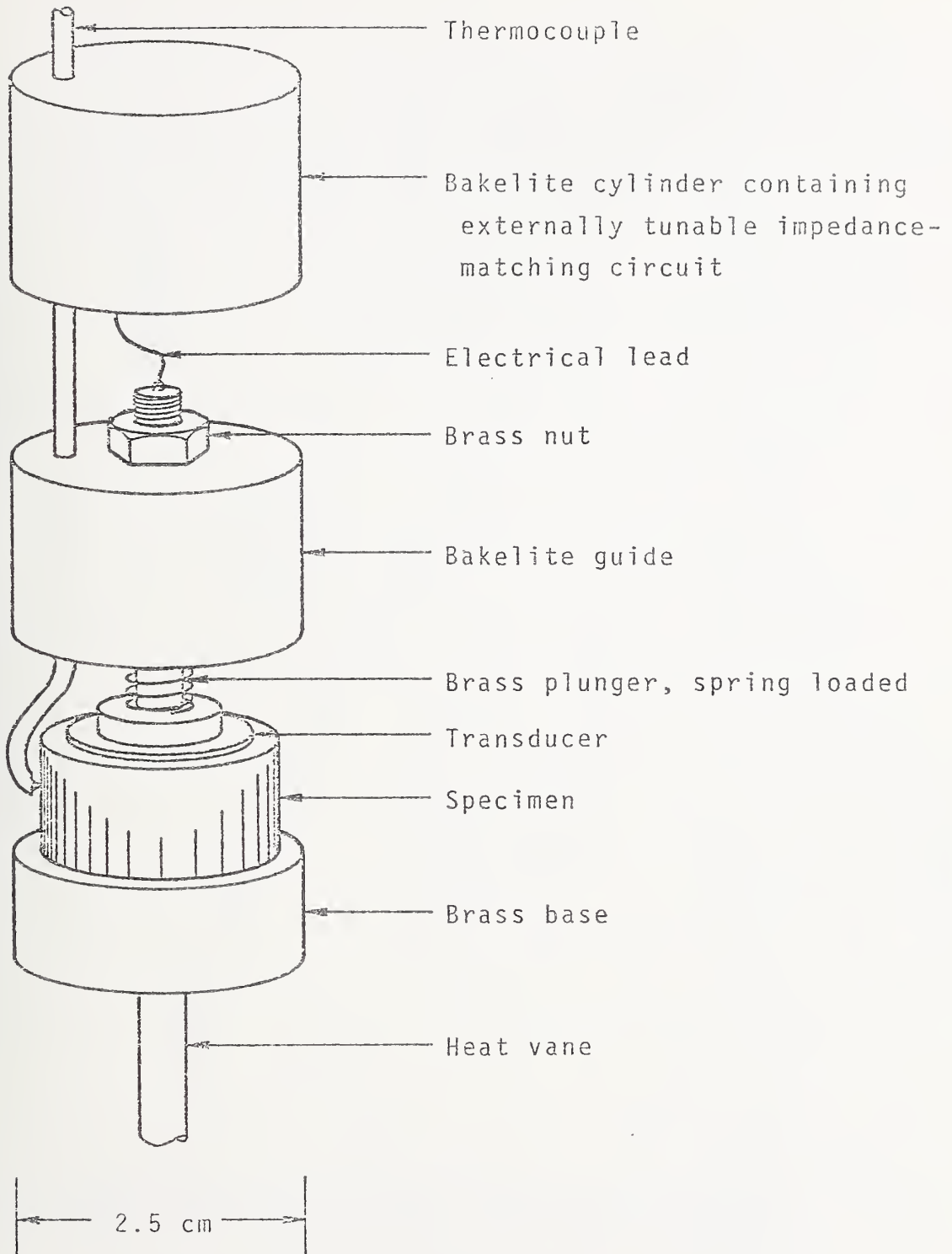
Table 4. Parameters in Equation 3

| Alloy       | Mode         | $C^o$<br>( $10^{11}$ N/m <sup>2</sup> ) | $C^s$<br>( $10^{11}$ N/m <sup>2</sup> ) | $t$<br>(K) |
|-------------|--------------|-----------------------------------------|-----------------------------------------|------------|
| Al5083      | $\rho v_l^2$ | 1.151                                   | 0.093                                   | 235.3      |
|             | $\rho v_t^2$ | 0.307                                   | 0.038                                   | 206.7      |
| Fe - 3.5 Ni | $\rho v_l^2$ | 2.763                                   | 0.140                                   | 246.7      |
|             | $\rho v_t^2$ | 0.840                                   | 0.053                                   | 218.7      |
| Fe - 5 Ni   | $\rho v_l^2$ | 2.687                                   | 0.230                                   | 353.8      |
|             | $\rho v_t^2$ | 0.819                                   | 0.104                                   | 345.8      |
| Fe - 6 Ni   | $\rho v_l^2$ | 2.692                                   | 0.244                                   | 380.5      |
|             | $\rho v_t^2$ | 0.835                                   | 0.125                                   | 398.7      |
| Fe - 9 Ni   | $\rho v_l^2$ | 2.663                                   | 0.126                                   | 252.7      |
|             | $\rho v_t^2$ | 0.799                                   | 0.057                                   | 246.0      |

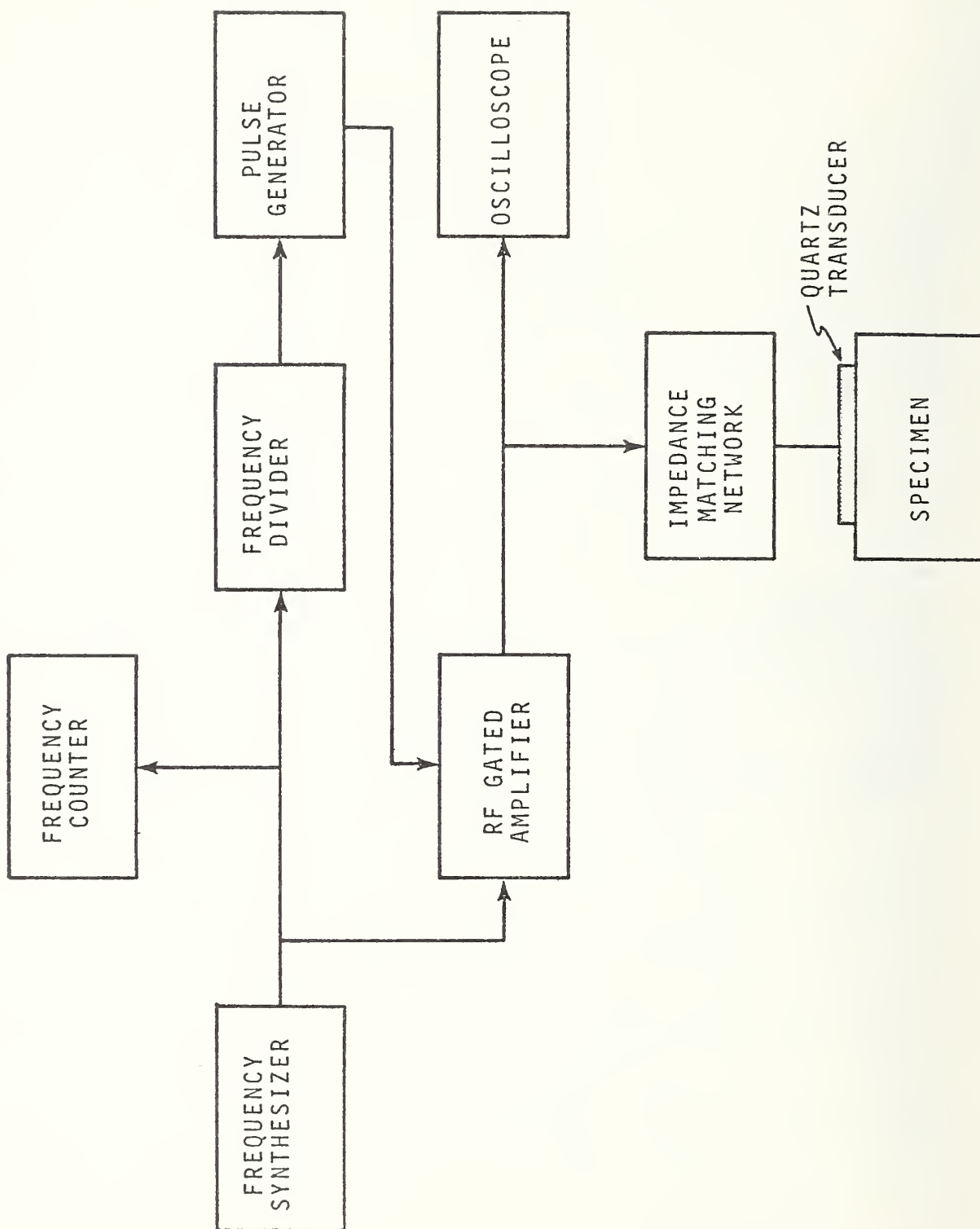
Table 5. Elastic Debye Temperatures at  $T = 0\text{ K}$

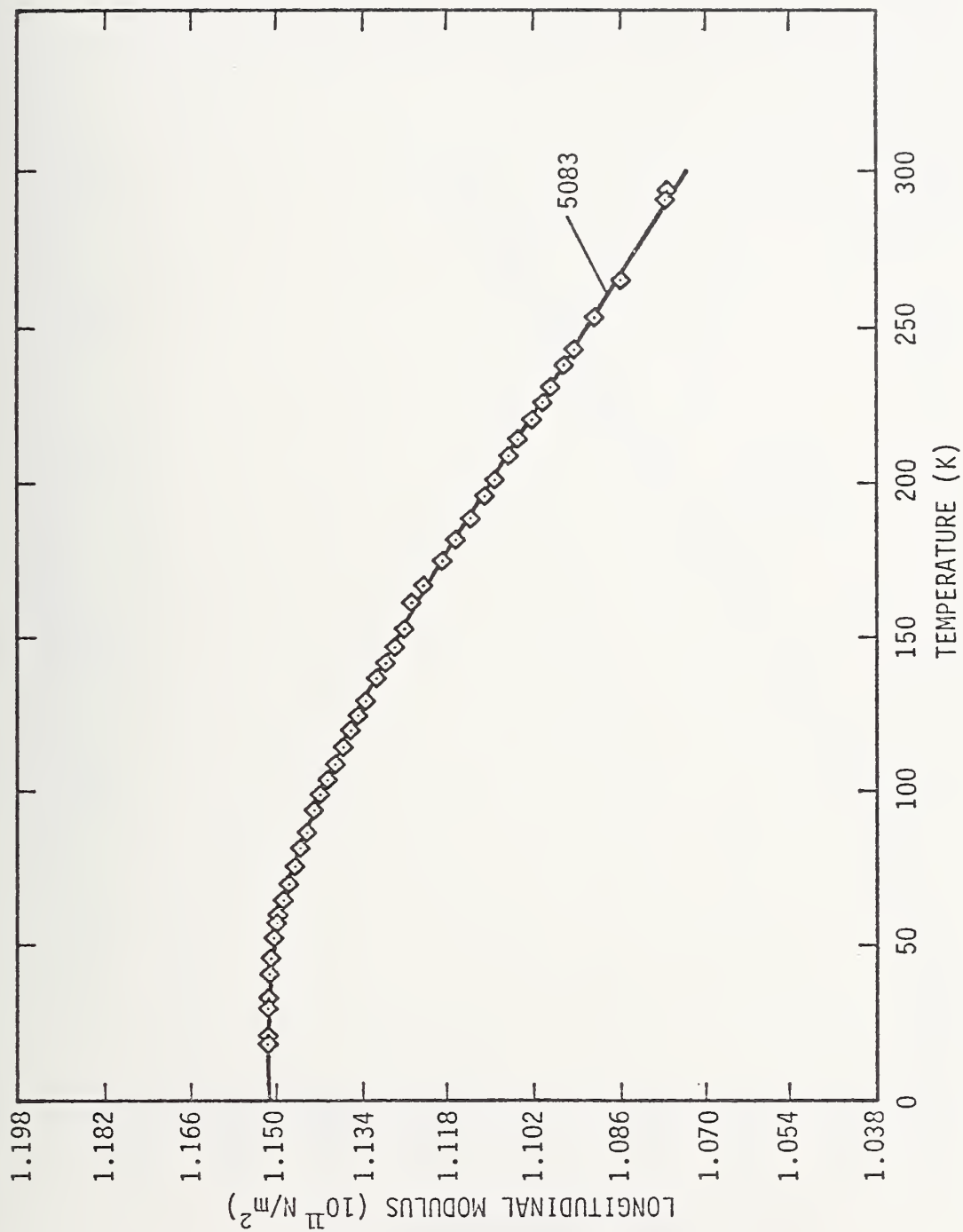
| Alloy       | $\theta$ (K) |
|-------------|--------------|
| Al 5083     | 414.8        |
| Al 1100     | 405.4        |
| Fe - 3.5 Ni | 463.7        |
| Fe - 5 Ni   | 459.0        |
| Fe - 6 Ni   | 463.4        |
| Fe - 9 Ni   | 453.0        |
| Fe *        | 477          |

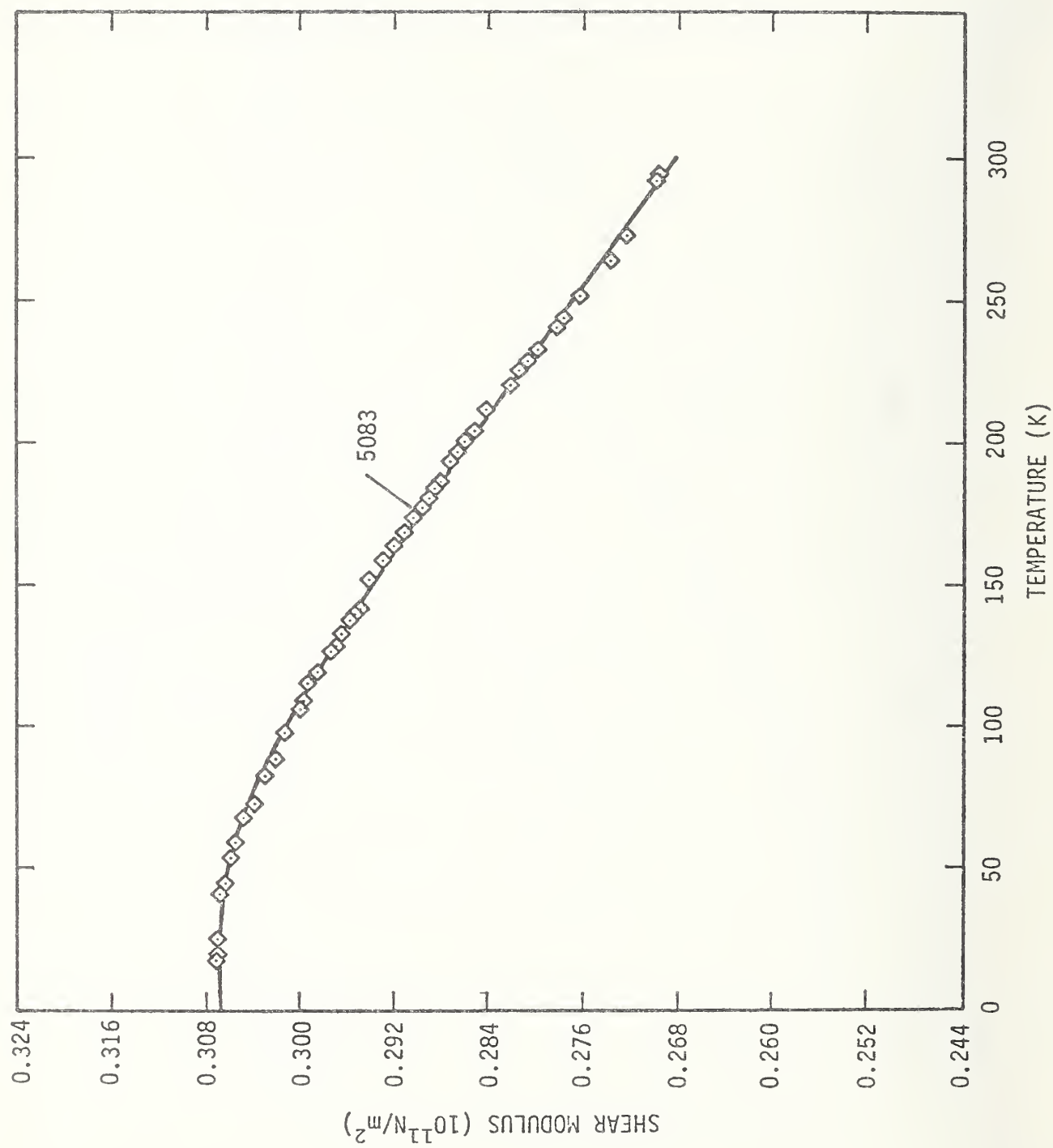
\* Reference 24.

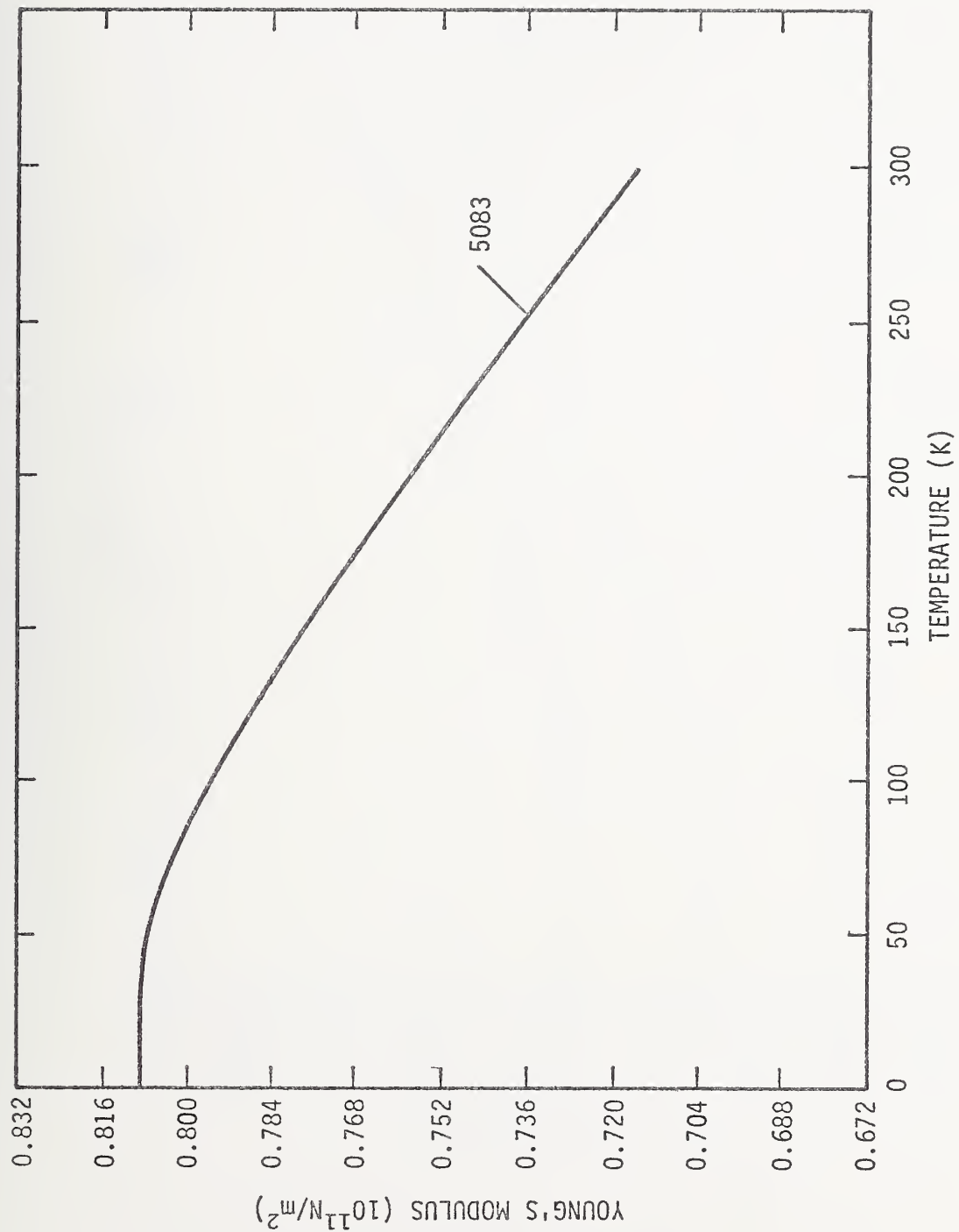


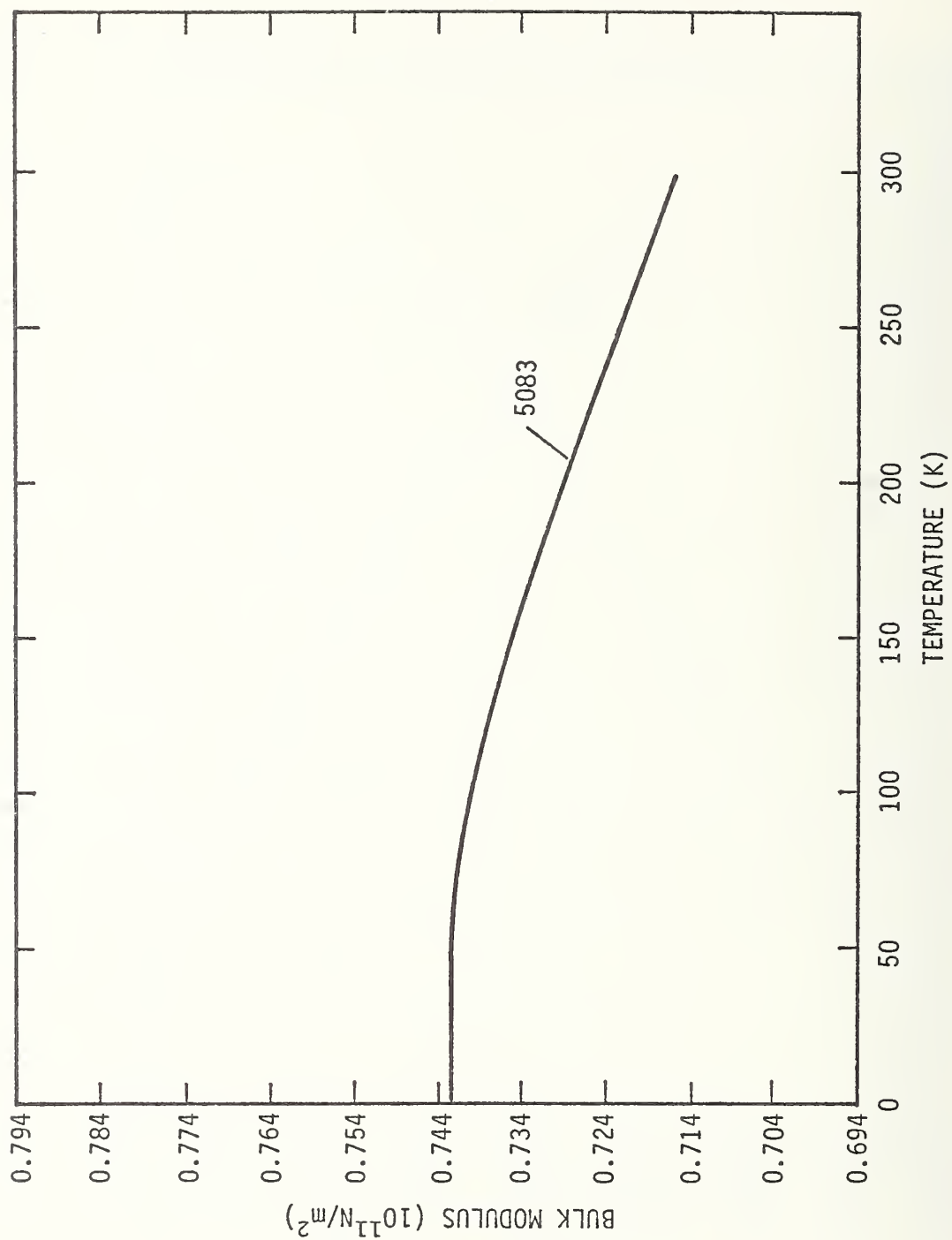




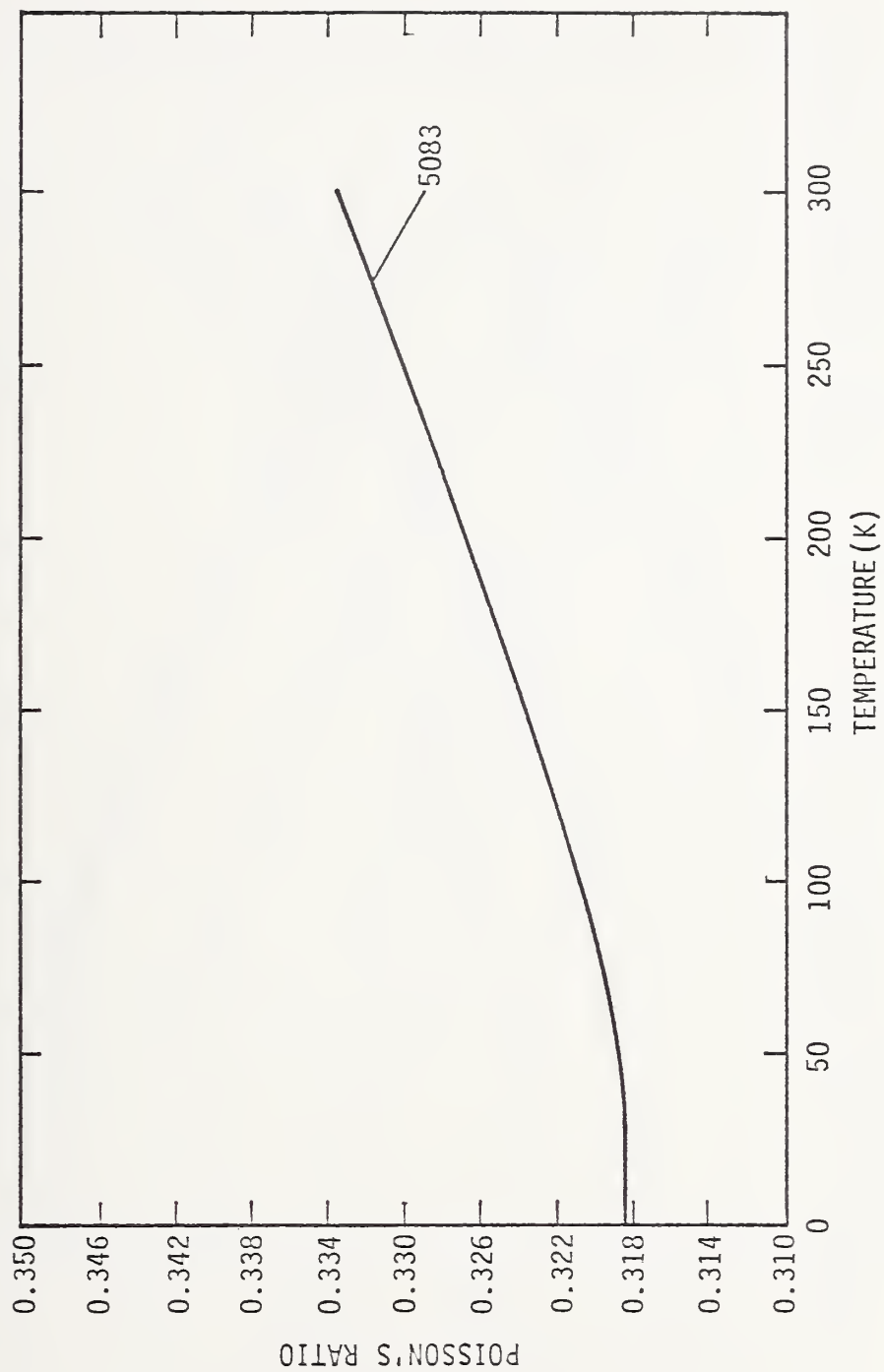


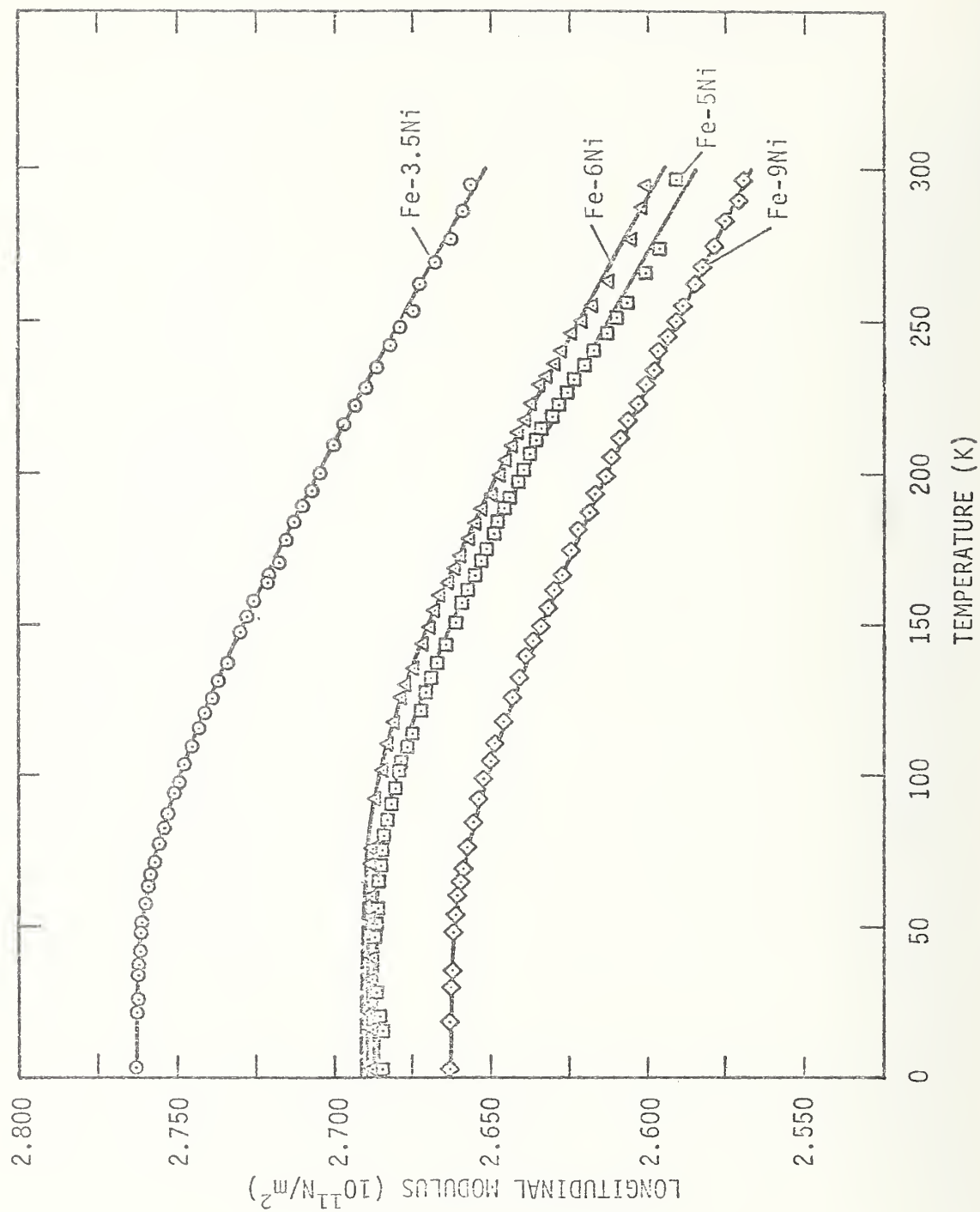


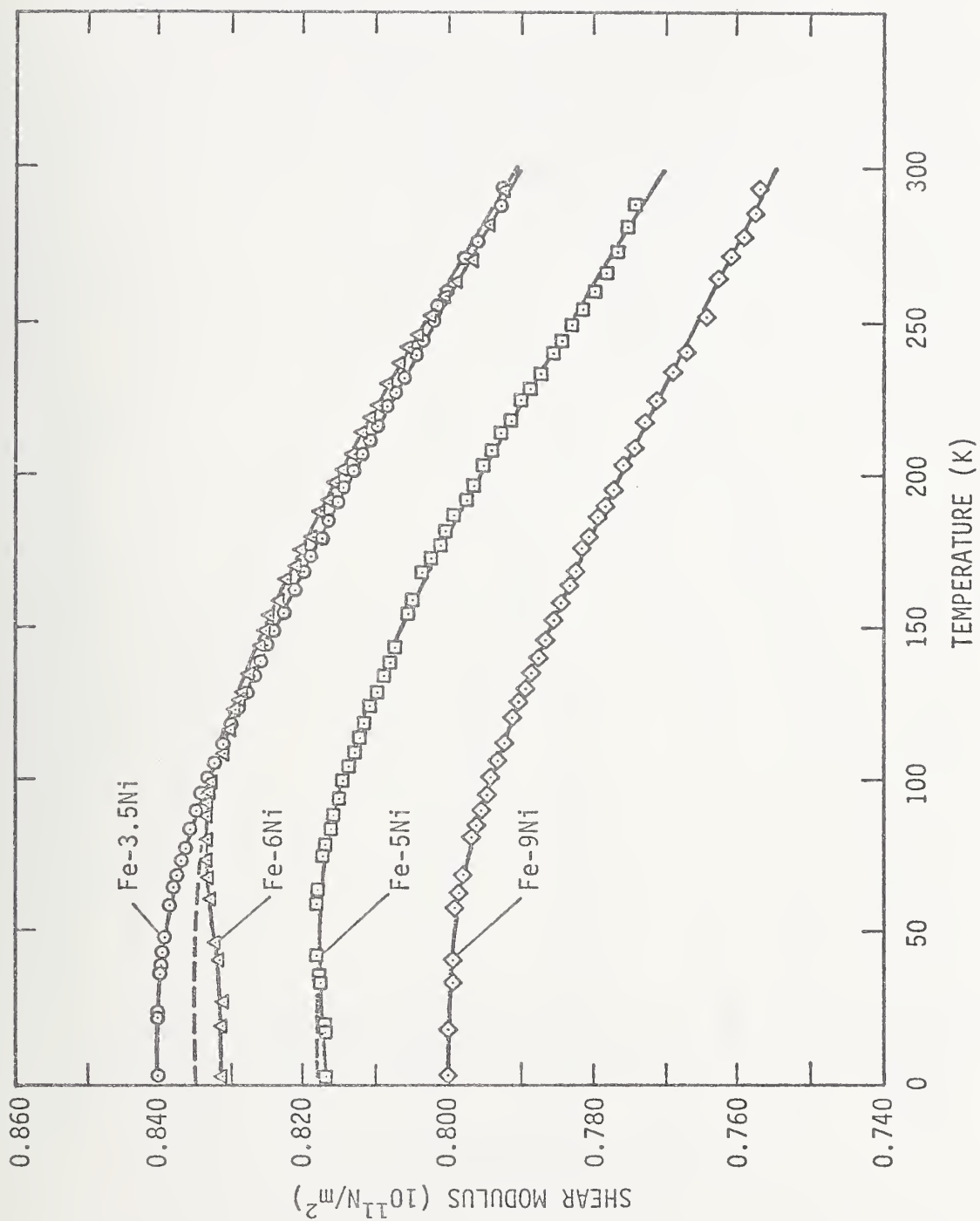


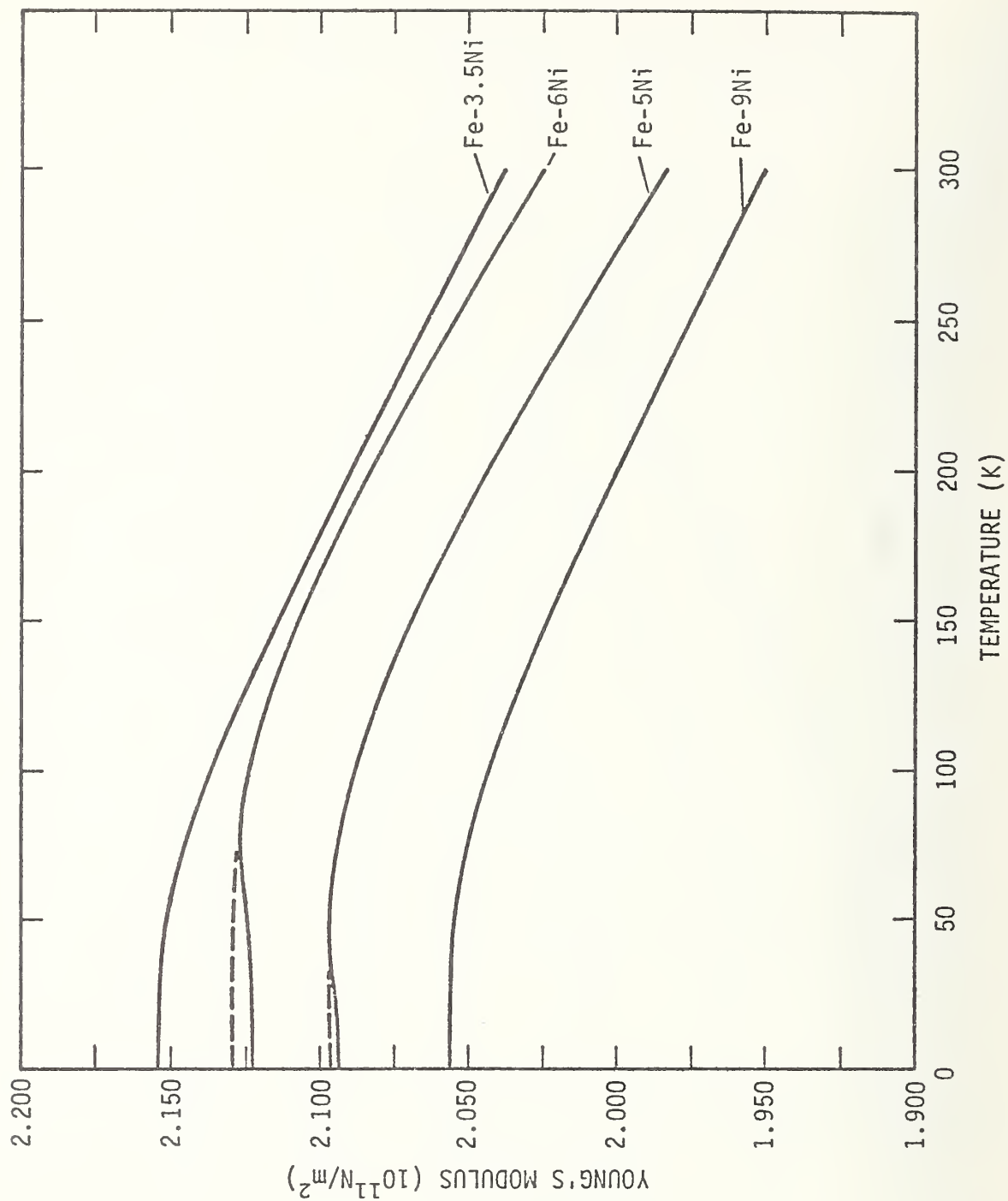


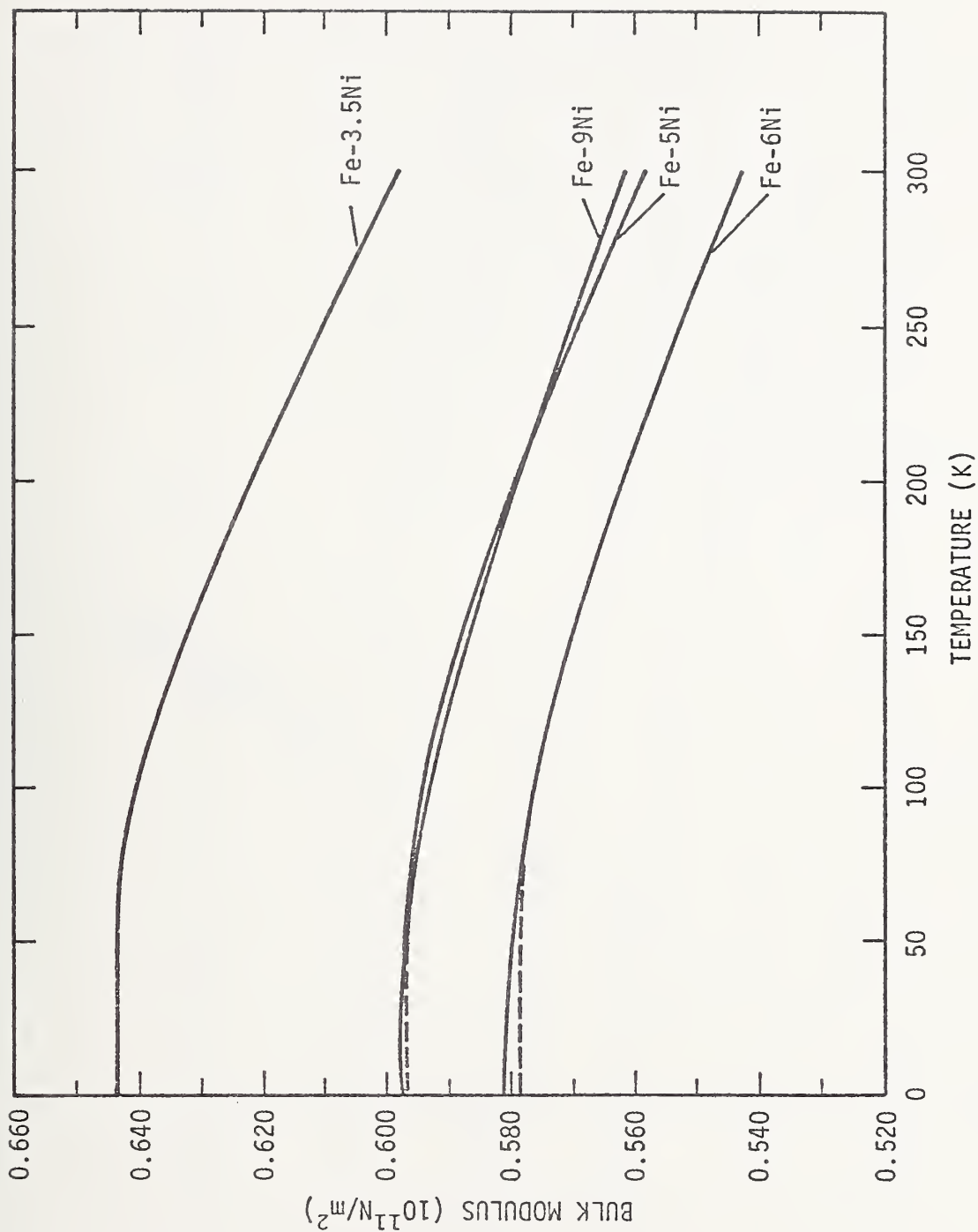




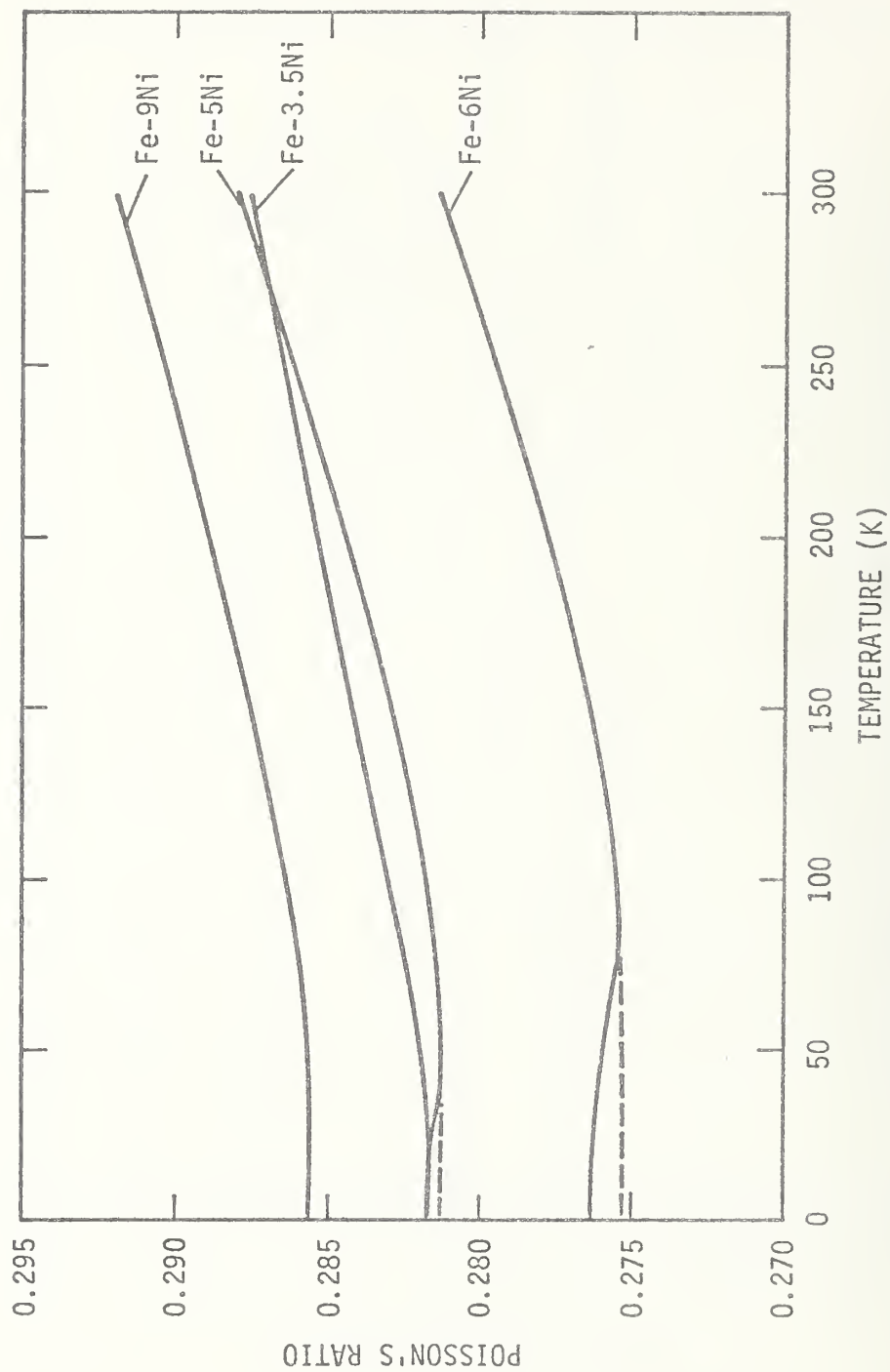




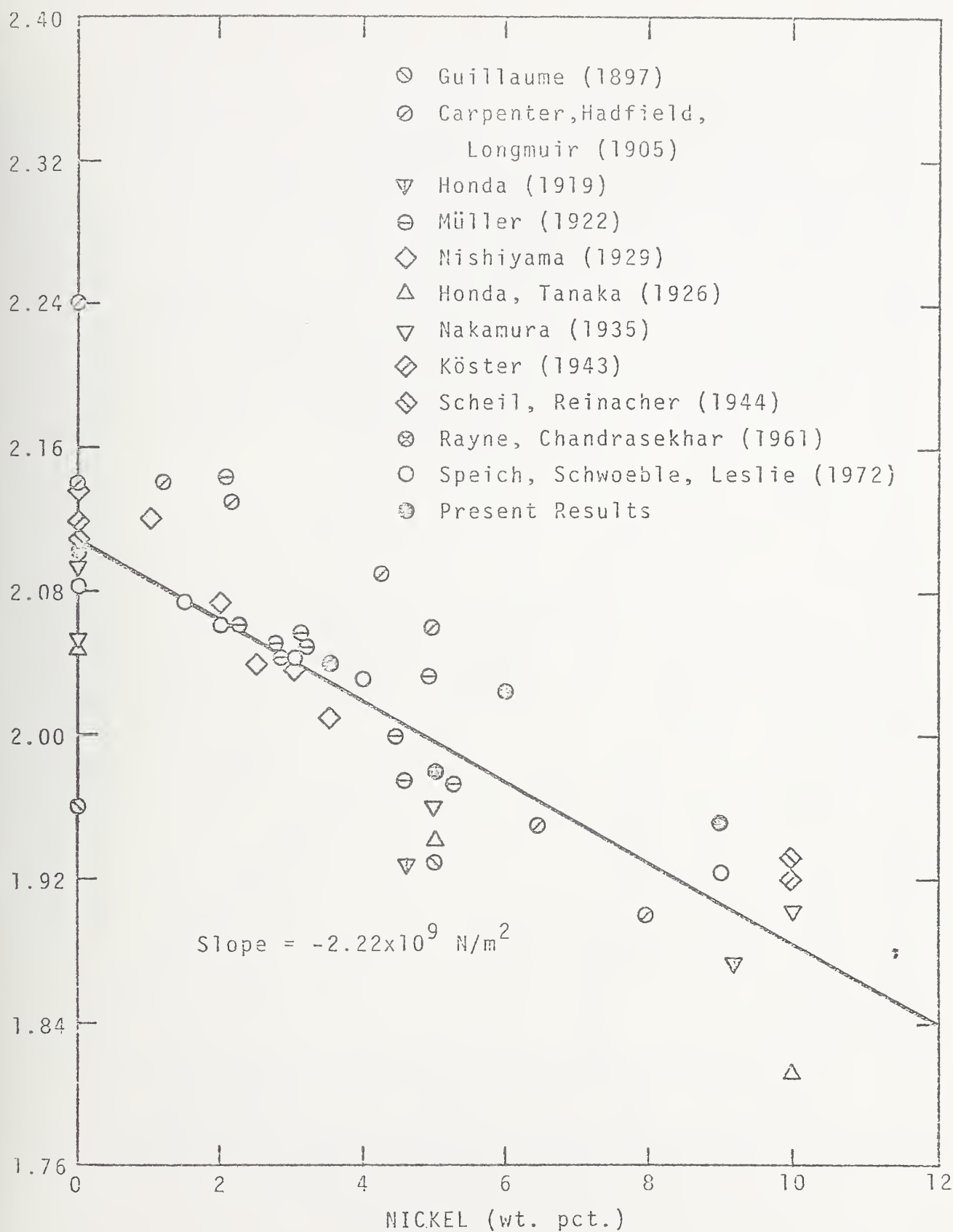


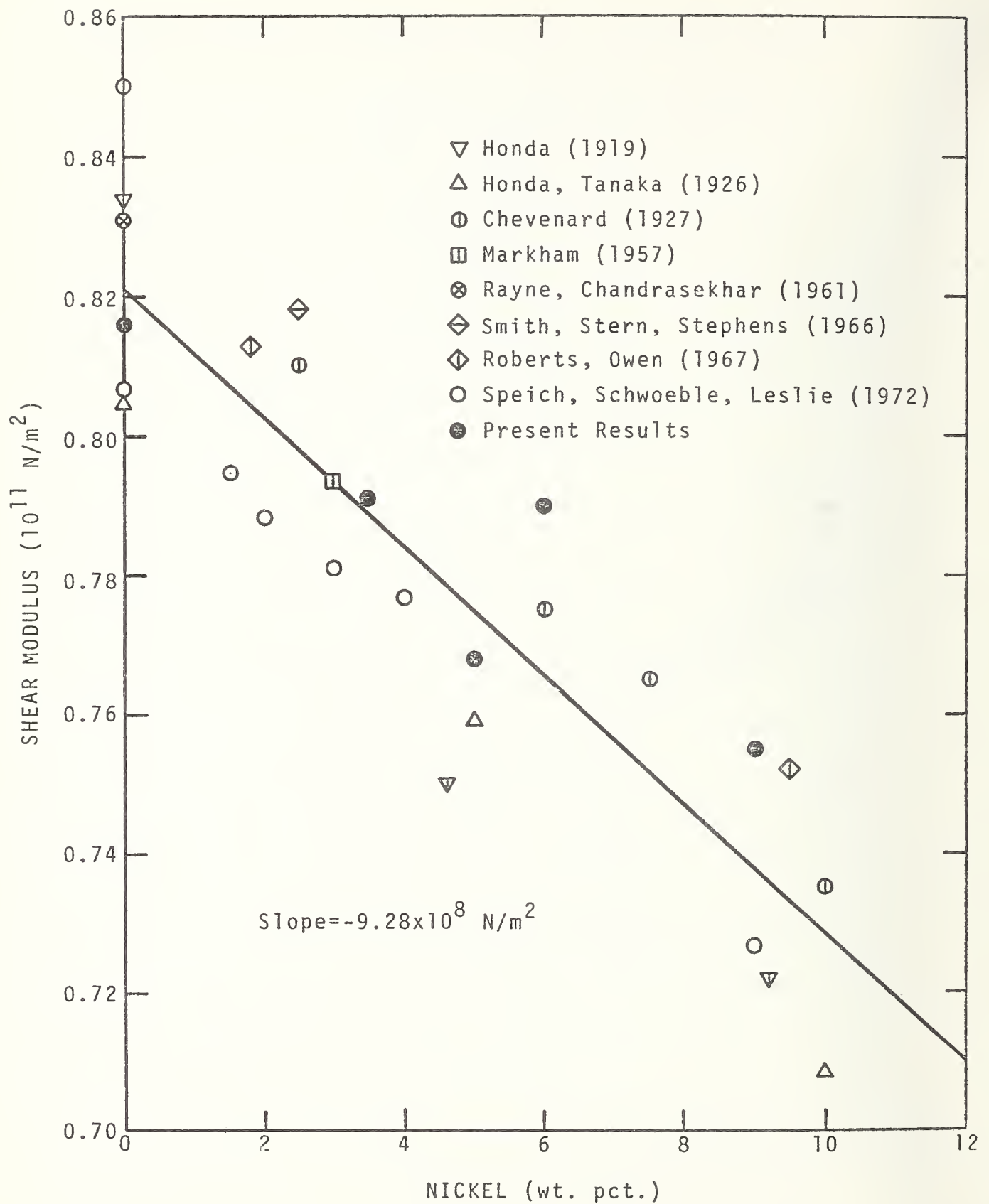


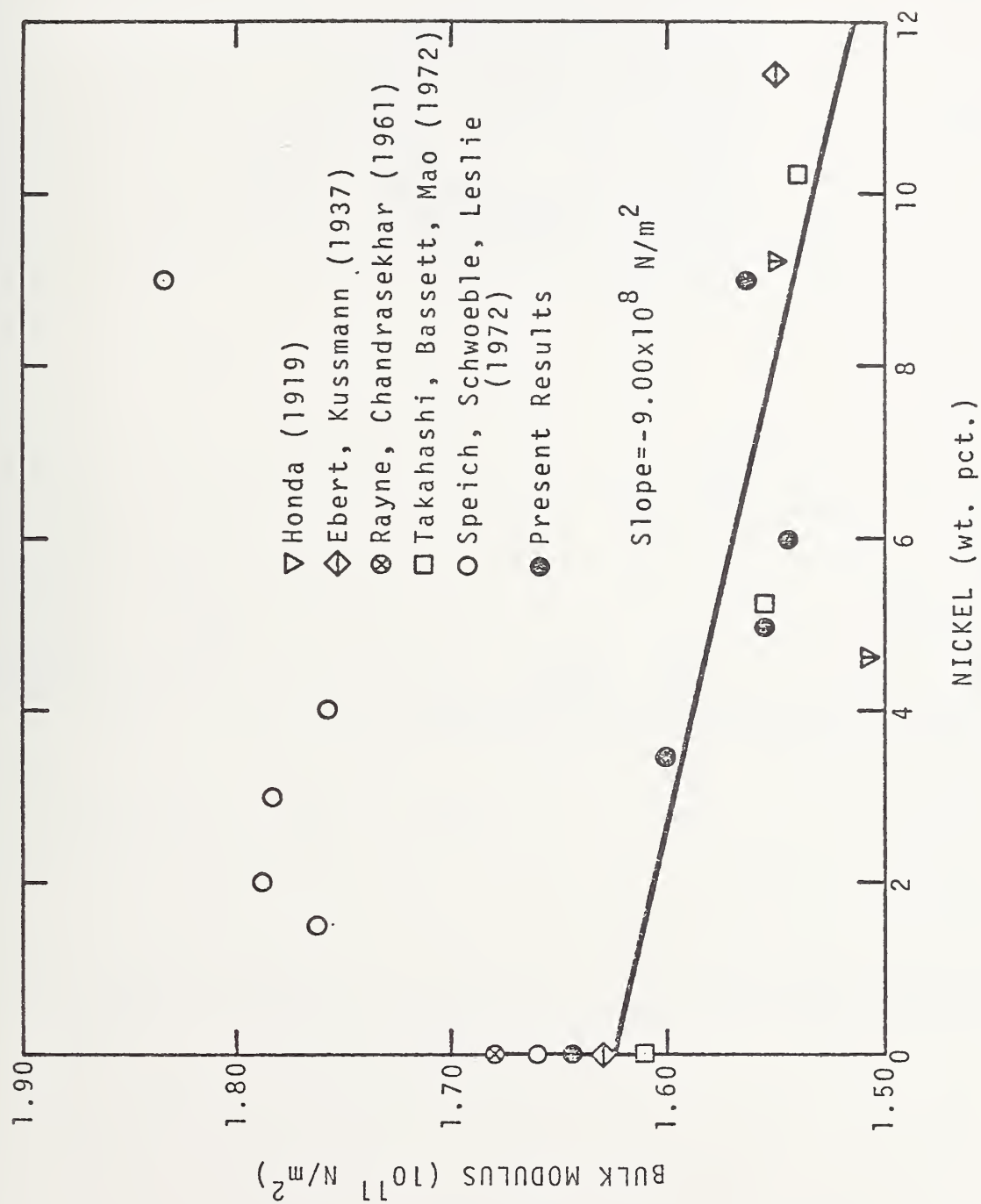


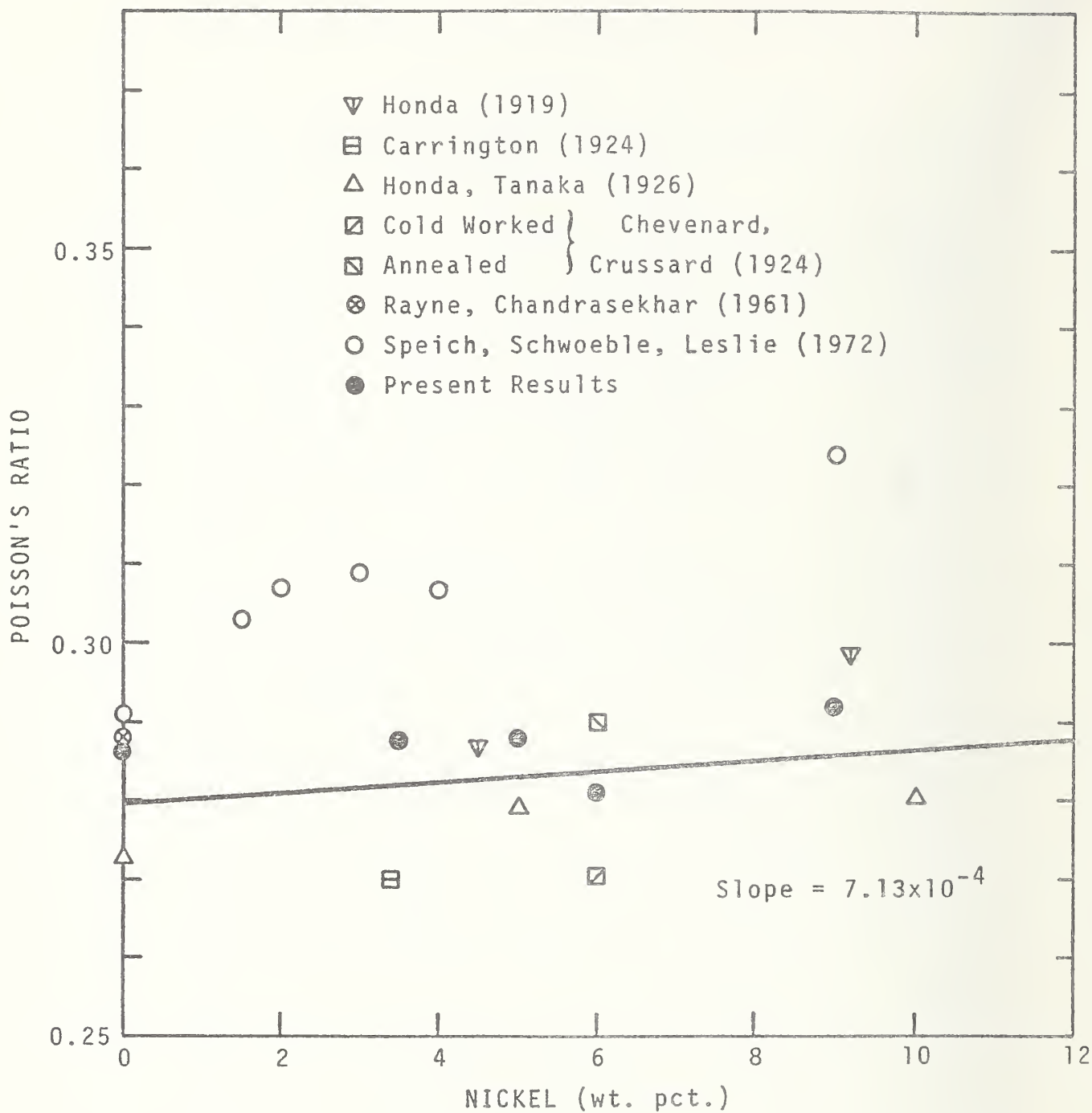


YOUNG'S MODULUS ( $10^{11}$  N/m<sup>2</sup>)











## APPENDIX O

A SURVEY OF LNG TECHNOLOGICAL NEEDS IN THE  
U.S.A. -- 1974 TO BEYOND 2000

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ABSTRACT

A comprehensive analysis of near and long term research needs has been conducted by the U. S. Gas Industry covering operational areas of Production and Exploration, Synthetic Supply, Transmission, Distribution, Utilization and LNG.

Identifiable research needs are reported for the area of LNG encompassing time frames of:

|             |                           |
|-------------|---------------------------|
| 1974 - 1978 | (In detail, year by year) |
| 1979 - 1985 | (In 5 year period)        |
| 1986 - 2000 | (As specific as possible) |
| Beyond 2000 | (As believed necessary).  |

A year by year examination of LNG research priorities for the first five years are considered vital to overcome the potential suppression of growth in the LNG industry that could result from lack of available technology. Assessments of technical LNG needs beyond 1978 cannot, of course, be too well defined and must be examined annually for purposes of updating.

The National Bureau of Standards Cryogenics Division has become the governmental focal point for LNG research. A survey of NBS LNG research and how these relate to the future technological growth of the LNG industry are discussed.

Paper presented at Fourth International Conference on Liquefied Natural Gas (Algiers, Algeria, June 24-27, 1974)

UN EXAMEN DES BESOINS TECHNOLOGIQUES DU GAZ NATUREL  
LIQUÉFIÉ AUX U.S.A. -- DE 1974 JUSQU' AU-DELÀ DE 2000

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RÉSUMÉ

Une analyse complète des besoins d'études, à court et à long terme, est menée par l'Industrie du Gaz des U.S.A. (U. S. Gas Industry) concernant les secteurs opérationnels de la Production et de l'Exploitation, de la Production Synthétique, de l'Acheminement, de la Distribution, de l'Utilisation et du Gaz Naturel Liquéfié (G.N.L.).

Les besoins de recherche dans le domaine du G.N.L. sont passés en revue pour les périodes suivantes:

|                 |                                     |
|-----------------|-------------------------------------|
| 1974 - 1978     | (En détail, année par année)        |
| 1979 - 1985     | (Pour la période de 5 ans)          |
| 1986 - 2000     | (Aussi précisément que possible)    |
| Au-delà de 2000 | (Ainsi que cela semble nécessaire). |

Un examen, année par année, des priorités de la recherche en ce qui concerne le G.N.L., est considéré comme vital pour les cinq premières années, afin de surmonter la stagnation potentielle de l'industrie du G.N.L. qui pourrait résulter d'un manque de disponibilité technologique. La répartition des besoins techniques du G.N.L. au-delà de 1978 ne peut évidemment pas être parfaitement bien définie et doit être examinée annuellement en vue d'une mise à jour.

La Division Cryogénique du Bureau National des Etalons (National Bureau of Standards Cryogenic Division) est devenue le centre officiel d'études du G.N.L. Un examen des études du Bureau National des Etalons ainsi que leur relation avec la future croissance technologique de l'industrie du G.N.L. sont discutés.

## A SURVEY OF LNG TECHNOLOGICAL NEEDS IN THE U.S.A. -- 1974 TO BEYOND 2000

The total energy needs of the United States are enormous and are continuously increasing. The nation's growing demand coupled with increasing concern for the environment, difficulties in meeting increased demand from traditional sources and current import uncertainties have led to shortages of all types of energy resources within the U.S. Between 1965 to 1970, the total U.S. domestic energy supply grew at a rate of 5% per year. Many energy economists now are foreseeing energy growth rates in the range of 4.1% to 4.8% per year during the 1970's [1].

The total energy consumed was  $44.8 \times 10^{15}$  btu in 1960,  $54.0 \times 10^{15}$  in 1965 and  $68.8 \times 10^{15}$  in 1970 (Figure 1). Assuming a total energy demand increase of  $4\frac{1}{2}\%$  per year,  $96 \times 10^{15}$  btu will be required during 1980 and  $122 \times 10^{15}$  btu by 1985. Natural gas, coal and oil were the primary resources of the energy consumed in residential, commercial, industrial and transportation sectors of the economy during 1973-74 (Figure 2).

The goal of the gas industry in the United States is to continue to provide a major portion of these future energy needs through the use of untapped natural resources, Canadian imports, synthesized fuel gas production from coal, oil shale, solid wastes, biomass, other natural resources and through the importation of LNG. The options and alternatives in support of this goal have been well defined -- what remains to assure future gas supply is the technological capability to find, produce and deliver this gas to the consumer by new or improved techniques and procedures.

The U. S. gas industry has the incentive and resources to meet this goal. It currently provides about one-third of the nation's total energy requirements. At the end of 1973, it served 43,700,000 residential, commercial and industrial customers through a 981,000 mile underground network of transmission and distribution lines. The gas industry has grown nearly twelvefold in terms of the book value of total assets since 1945, expanding from a 5 billion dollar industry to more than 59 billion dollars at the end of 1973. Preliminary figures for 1973 show a total consumption of  $22\frac{1}{2}$  trillion cubic feet (637 billion cubic meters). The total annual gas requirements in the U. S. are expected to increase to 46.7 trillion cubic feet (1.32 trillion cubic meters) by 1990 as shown in Figure 3.

In the U. S., as in every industrialized nation of the world, the demand for natural gas is increasing. The growing intensity of the worldwide shortages over the past year has touched off a global scramble to obtain supply agreements with producing nations and arrange for construction of related facilities. In the U. S. alone some 10 LNG import terminals [2] are under construction or planned at a cost of almost 1 billion dollars per facility. Each liquefaction complex

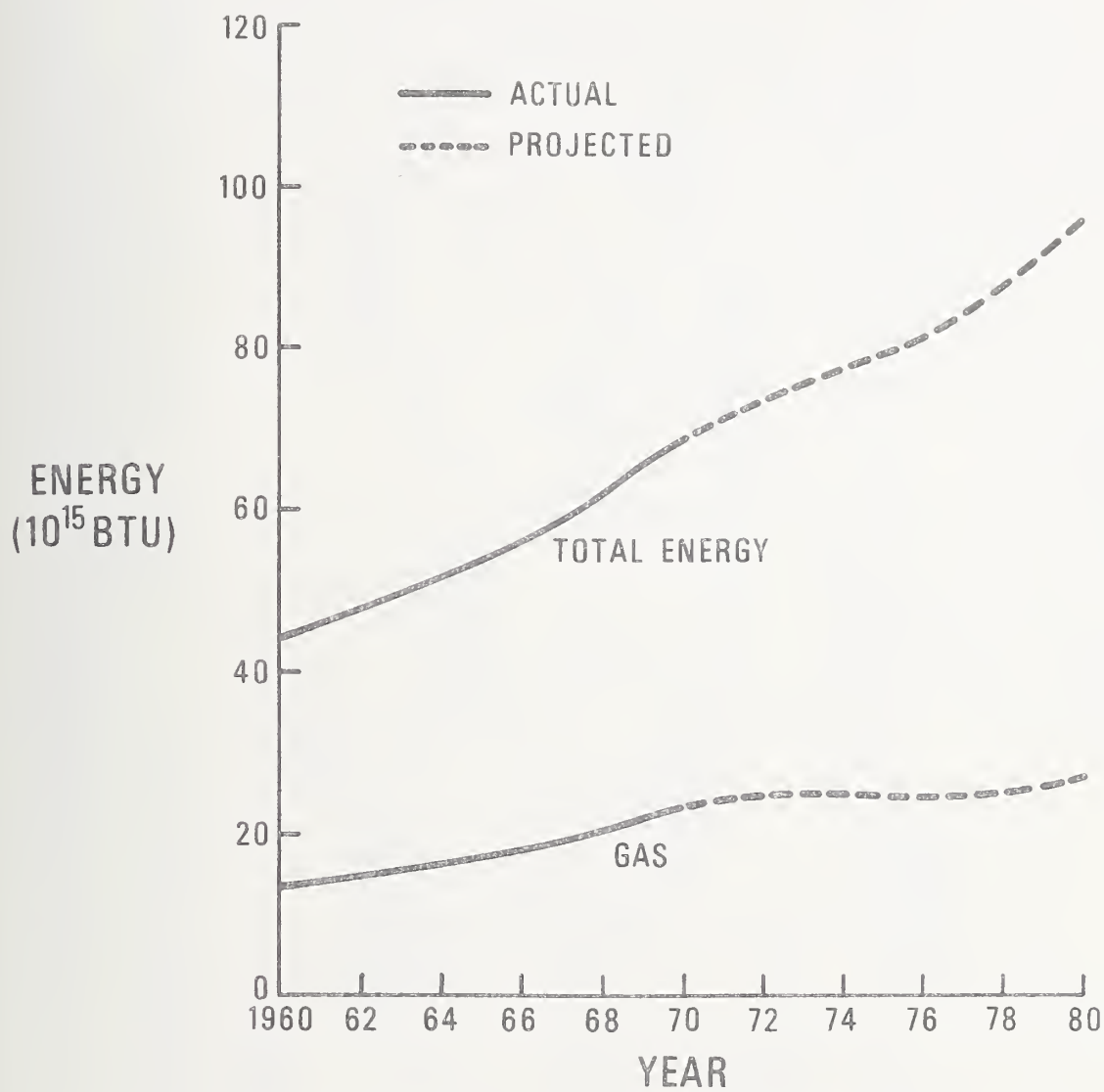
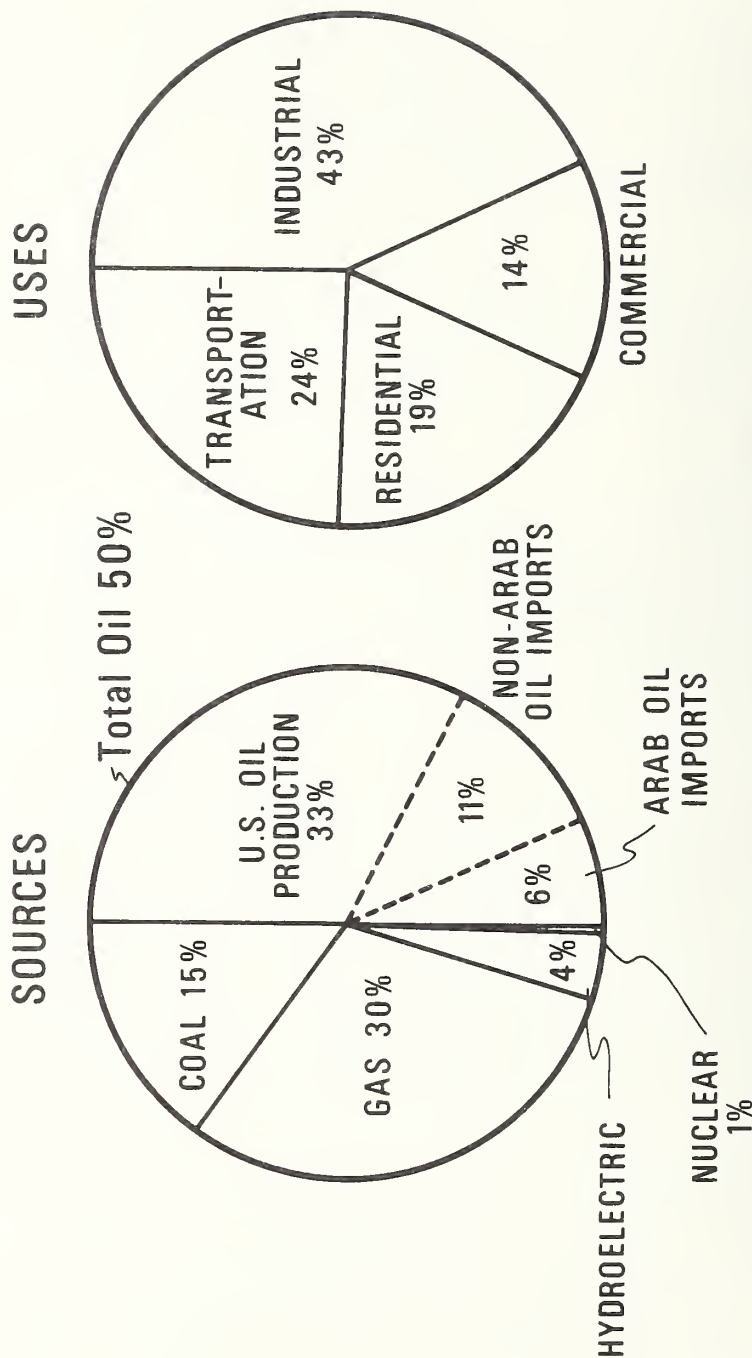


Figure 1. Energy consumption in the United States.



# U.S. Energy Sources & Uses

## Winter 1973-1974



UNCERTAIN SOURCES 8% OF TOTAL  
(2-3 MILLION BARRELS PER DAY)\*

\*POSSIBLE SHORTAGE WHICH MUST BE OVERCOME THIS  
WINTER & FOR WHICH INCREASED DOMESTIC SOURCES  
MUST BE DEVELOPED FOR FUTURE USE.

Figure 2.

# *Future Gas Consumption of the United States*

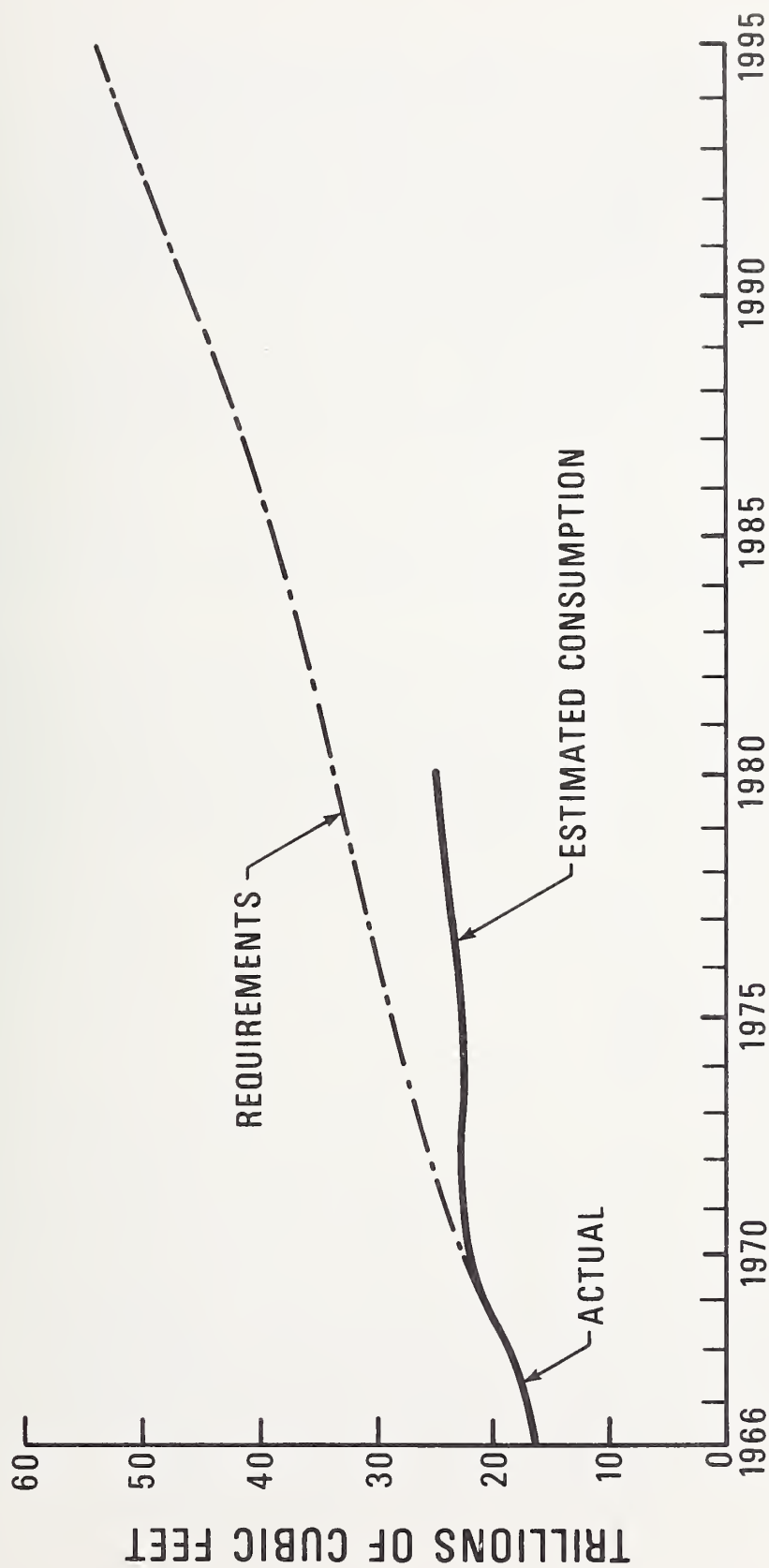


Figure 3. Future gas consumption of the United States.

accounts for approximately \$300 million with the remainder of the \$1 billion going for ships, pipelines, receiving terminals and storage facilities.

Supplemental gas supply projections for the period 1972-1990 prepared by A. G. A. forecast an LNG importation of 3.2 trillion cubic feet (91 billion cubic meters) by 1990. This projection (Table 1) represents 20% of the total estimated supplemental supply. This thousand-fold increase over the two billion cubic feet (57 million cubic meters) imported during 1972 demonstrates the massive dimension of the rapidly emerging LNG market in the U. S. alone. LNG technology has created a truly international gas industry.

It is axiomatic that this growing section of international gas operations be supported by a comprehensive, continuing research effort to assure energy conservation and safety of all elements, liquefaction, transportation, transfer, storage and plant operation.

Over the past year, the Natural Gas Industry has placed an accelerated emphasis on viewing its supply in relation to projected demand, the reasons for that demand and identification of future technological needs required to balance supply and demand.

Based on an awareness of the role played by Research and Development in furnishing the required advanced technology to assure continued supply and growth, the U. S. Natural Gas Industry undertook a comprehensive study to define the requirements for future research and development and formulated an R&D plan that would assist the gas industry to help satisfy the nation's future energy needs. This study [4] was structured to examine in detail the needs for research and development in each of six major areas, namely

- Exploration and Production
- Synthesized Natural Gas (SNG)
- Transmission
- Distribution
- LIQUEFIED NATURAL GAS
- Utilization

The basic technology required to import LNG exists today (no major technology "breakthrough" required). However, to respond to the rapidly changing demands for energy in all forms, a major research activity has been identified for the gas industry as necessary at this time to accelerate development of this market. The technology involved in ship transportation and large-scale liquefaction is being pursued aggressively and adequately by groups of companies with large financial commitments. We recognize, however, that many items of the research plan program we have recommended will impact on the development programs being conducted by companies outside the gas industry. Coordination between these various R&D programs is essential, therefore, particularly in such areas as LNG ship design and the configuration and construction of marine terminals.

TABLE 1.

*Planning Division - A.G.A.  
Supplemental Gas Supply Projections (10<sup>12</sup> cubic feet)  
November 1973*

| SOURCE                      | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1980 | 1985 | 1990 |
|-----------------------------|------|------|------|------|------|------|------|------|------|
| Alaskan Imports             | —    | —    | —    | —    | —    | —    | 0.6  | 1.5  | 2.4  |
| Canadian Imports*           | 1.0  | 1.1  | 1.2  | 1.3  | 1.4  | 1.5  | 1.8  | 2.4  | 3.0  |
| LNG Imports                 | Nil  | Nil  | Nil  | 0.2  | 0.4  | 0.7  | 1.7  | 2.7  | 3.2  |
| Oil Gasification            | —    | Nil  | 0.2  | 0.6  | 1.1  | 1.4  | 1.7  | 2.2  | 2.2  |
| Coal Gasification           | —    | —    | —    | Nil  | Nil  | 0.2  | 0.4  | 1.3  | 2.8  |
| Advanced Fracturing         | —    | —    | —    | —    | —    | Nil  | 0.1  | 0.8  | 1.5  |
| Total Supplemental Supply** | 1.0  | 1.1  | 1.4  | 2.1  | 2.9  | 3.8  | 6.3  | 10.9 | 15.1 |

\*Bureau of Mines 1972 new receipts from Canada

\*\* Supplemental supplies are defined as those which add to lower 48 states natural gas production

Seven critical research needs were selected for immediate study. These items generally cover the metrology and the safety aspects of liquefied natural gas transport, transfer and storage.

This plan also recommends an additional allocation of research funding on an unassigned basis; the rapid changes occurring in the overall LNG picture will undoubtedly create new demands for research. Total cost of the R&D program to meet the essential needs is estimated to be almost \$13 million (Figures 4 and 5).

The LNG research plan includes the results of an industry-wide poll of LNG research needs, both foreign and domestic. Based on the responses to this poll, an original group of some forty-two research needs were defined and identified. It was obvious that many of these research needs were being, or should be undertaken by manufacturers, perhaps with the cooperation of the gas industry. Many of these topics are listed in Table 2.

The LNG plan identified four research projects that could properly be categorized as long-range research (beyond 1980) needs; long distance LNG transfer lines, novel LNG transport methods, improved concepts of LNG storage, and utilization of LNG refrigeration.

These tasks were suggested to provide a more definitive answer to constantly recurring questions such as: are long-range LNG pipelines really feasible and economic? ; are there really any new concepts for LNG storage or transportation? ; can the refrigeration available from LNG be utilized practically and economically?

It is recognized that specific LNG research is being sponsored by many segments of the International LNG Industry. These efforts are applauded and are expected to continue as the LNG market continues to grow. It is our purpose, however, to recognize and identify those research areas that can impact upon and re-enforce the many individual LNG research efforts underway or planned by the various elements of the LNG industry. Communication internationally between the various programs as exemplified by LNG-4 is deemed essential to assure an orderly and effective worldwide growth in LNG trade.

The National Bureau of Standards, having played a vital role in past LNG research in support of the gas industry plan, has a number of programs underway that are of importance to the future of the LNG industry.

#### LNG RESEARCH AT NBS

As the LNG industry has matured from concept through demonstration projects to full scale peak shaving, satellite and base load operations, the requirements for information necessary for implementation of current and future LNG application have been significant. This required information exists in many forms, including data for equipment design, decision making



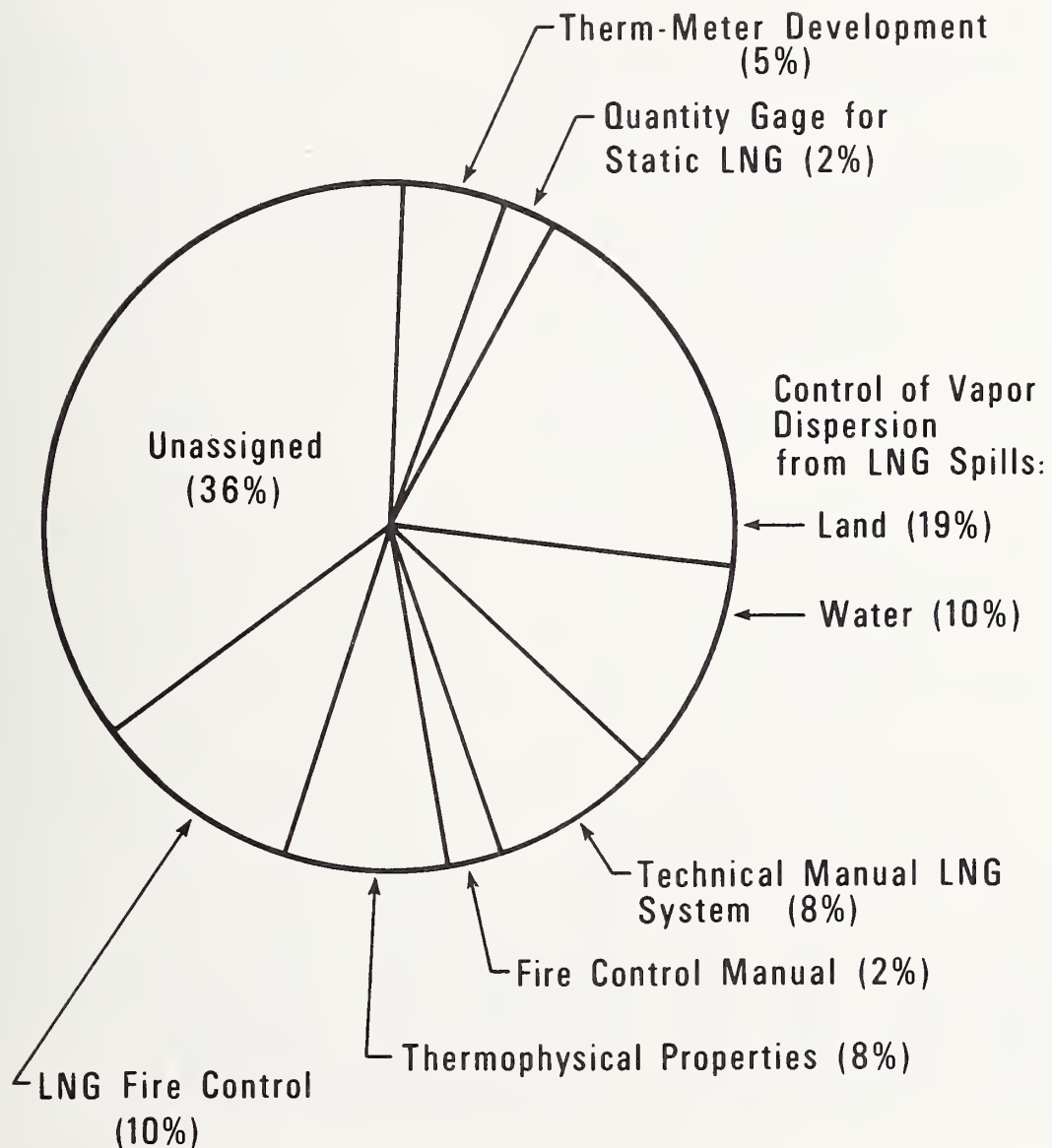


Figure 4. Allocation of LNG research and development costs - first five years [4].

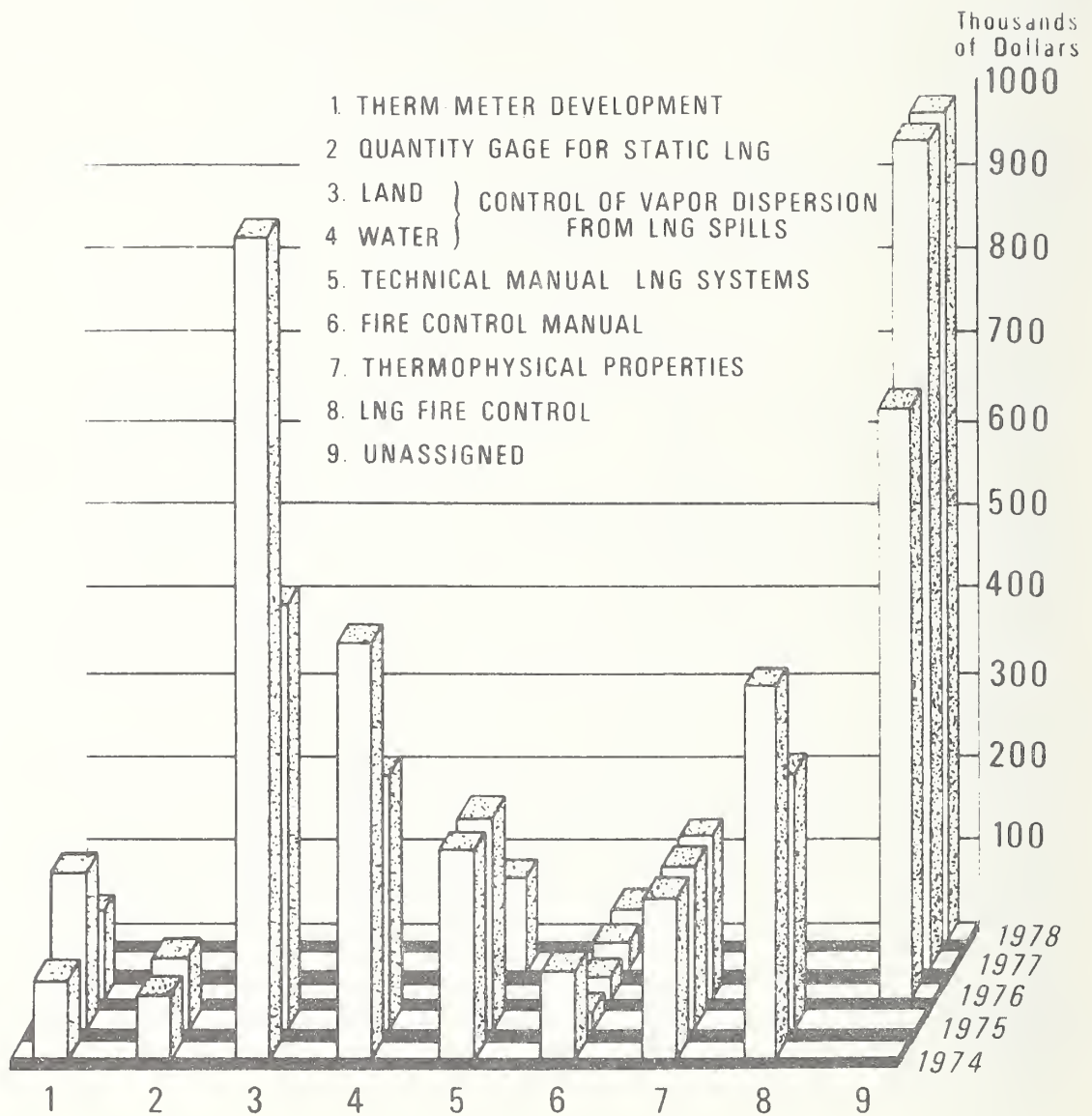


Figure 5. Annual LNG research and development funding [4].

TABLE 2.  
SECONDARY LNG RESEARCH TASKS -- AGA  
GAS RESEARCH PLAN [4]

|                                                                 |                                                                                                               |
|-----------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| LNG Facility Siting Criteria                                    | Processing Improvements                                                                                       |
| Definition of standards and codes                               | Improved liquefiers, vaporizers, etc.                                                                         |
| Risk analysis                                                   | Limits of water, CO <sub>2</sub> and other trace contaminants as a function of onstream time without deriming |
| Analysis of hazards to LNG from adjacent facilities             | Thermal and chlorine pollution of cooling water                                                               |
| Environmental impact of LNG (cold, vapor and fire)              |                                                                                                               |
| Flame detection systems                                         | Long Range Research Area                                                                                      |
| Properties of Materials Used in LNG Service                     | Short Distance LNG Pipelines                                                                                  |
| Insulation research                                             | Review existing files and literature to search for new technology                                             |
| Structural materials                                            |                                                                                                               |
| Other materials                                                 | Other                                                                                                         |
| LNG Transportation Systems Research                             | LNG conservation research                                                                                     |
| Development of new ship unloading concepts                      | Effect of SNG and imported LNG on peak shaving LNG operations                                                 |
| Reliquefiers for ships                                          | Static electricity in plants and ships: sources, effects, methods of preventative design                      |
| Risk analysis re: storage, tanks, equipment                     | Earthquake design                                                                                             |
| Purge of LNG transfer systems                                   | Effects of LNG spill on outer, non-cryogenic hull plate of tanker                                             |
| Develop effective, quick shut-down systems (e.g., water hammer) | Tanker disturbance of shore and bottom life in shallow canals                                                 |
| New concepts in moorings                                        | Contingency plans for LNG industry                                                                            |
| Supertanker port                                                |                                                                                                               |
| Supmarine pipeline                                              |                                                                                                               |
| Economics of long distance transport                            |                                                                                                               |
| Ship construction and strength during collision                 |                                                                                                               |

(which process to choose), commodity transfer (providing equity in trade), data for safety applications as well as information for local, state, federal and international codes and standards, preparation of environmental impact statements and data for establishing insurance rates and financial considerations.

Certain well defined areas of required information fall within NBS traditional roles in this specialized field of cryoengineering and cryophysics. It was believed that NBS could combine both leadership and supportive roles to other government agencies and industry by (1) providing physical data of national importance not previously available in sufficient accuracy, (2) measurement methods, test methods and instrumentation, (3) standard assistance to voluntary and regulatory standardizing bodies, and (4) innovative technological leadership in methods and systems to reduce losses in transport and storage and to provide necessary expertise to facilitate and reduce the time required for program implementation.

Historically, NBS, through its Cryogenics Division in Boulder, Colorado, has supported government and industrial programs in cryoengineering and cryophysics since 1952. Concerted efforts in the general field of liquefied natural gas were begun in 1968. Currently, our program (having 14 elements or parts) provides the content of liquefied natural gas technology at NBS and is supported by a group of government agencies and industrial organizations (Table 3) which have a broad range of requirements. For purposes of explanation the 14 programs can be categorized into three more or less traditional NBS areas -- reference data, measurement science, and technology transfer.

#### Reference Data

By 1965 programs involving liquefied natural gas had demonstrated its viability as a peak shaving, satellite and supplemental fuel. Requirements for property data included PVT relationships, enthalpy, entropy, internal energy, dielectric properties, specific heats, heats of vaporization, speed of sound and the transport properties of viscosity, thermal conductivity and thermal diffusivity. Properties data were available from a number of sources and, where useful for certain purposes, were found to be insufficient for future planning, inadequate for many process designs and of either undefined or of inadequate precision and accuracy. What was needed therefore were accurate precise reference data over a broad range of pressures and temperatures generally extending from near the triple point of methane to well above ambient conditions. LNG presented an additional challenge since it is a non-ideal mixture of five or more hydrocarbon fluids and nitrogen, and the LNG mixture fraction will vary with source, time and storage treatment. The reference data must be of such quality as to classify it as basic reference values where foreseeable advances in measurement technology would not materially affect the listed values.

TABLE 3.  
LIST OF AGENCIES AND COMPANIES CURRENTLY SUPPORTING  
LNG RESEARCH AT NBS

U. S. Department of Commerce

National Bureau of Standards  
Maritime Administration

American Gas Association, Incorporated

Pipeline Research Committee (AGA)

U. S. General Services Administration

U. S. Federal Power Commission

LNG Density Committee consisting of:

El Paso Natural Gas  
Tennessee Gas Pipeline  
Distrigas Corporation  
Columbia Gas Service Corp.  
Gaz de France  
Natural Gas pipeline Company  
Easco Gas LNG, Incorporated  
Transcontinental Gas Pipe  
Line Corporation

Chicago Bridge & Iron Company  
Shell International Gas, Ltd.  
Sonatrach  
Southern California Gas Company  
Phillips Petroleum Company  
Texas Eastern Pipeline Company  
Marathon Oil Company  
Mobil R&D Company  
Tokyo Gas Company, Ltd.



A comprehensive program including both interim and long term objectives is currently in progress. The interim program involves the definition of densities of LNG as a function of pressure, temperature and mixture fraction. A 17 company committee is participating in the development of these accurate data of liquefied natural gas mixtures to provide a basis for custody transfer methods and equitable custody transfer agreements. The program will provide a data base for mass and density gauging. The objective of this LNG density measurement program is to provide accurate (0.1%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures, mainly in the temperature range 90-150 K, at pressures to 10 atmospheres. Measurements are in progress and will include six pure components, about 60 binary mixture compositions, and about 13 multicomponent mixture compositions. A high precision (0.05%) magnetic densitometer (based on Archimedes Principle) has been designed and constructed and is in the final stage of proving. The program is in its second year of operation with anticipated completion in 1975.

The long term fluids program involves a wide range of properties in addition to density. In general, the pure components of LNG are being studied and analyzed extensively over broad ranges of pressure and temperature, and then mixture laws applied or developed and confirmed with experimental verification. An example of this approach is the recently completed program on pure methane. Prior to 1970, interest in methane was general and was primarily directed to pure methane considered as a cryogenic fluid [5-17]. Several progress reports were published by Goodwin [18,19] and the final report is now available [20]. This latter report includes extensive physical properties data for methane such as fixed point constants, melting line, vapor pressure, orthobaric densities, virial equations, equation of state, specific heats, heats of vaporization and speed of sound. In addition, derived properties of entropy, enthalpy, and internal energy are included along with detailed explanations of computational methods including computer programs. Tabular data in both SI and British Units are also provided with estimates of uncertainties of all data. Figure 6 shows pressure and temperature boundaries of properties described by Goodwin.

It is acknowledged that this publication of the thermophysical properties data is not necessarily in the form most useful for engineering applications. Various charts and graphs will be required as well as other data forms of lessor or greater detail. This major three-year program has produced what we believe to be "best value" reference data on the major component of LNG.

The work on methane has also resulted in publication of accurate dielectric constants data for pure, compressed and liquefied methane [21]. This data should prove useful in providing a data base for mass and density gauging.

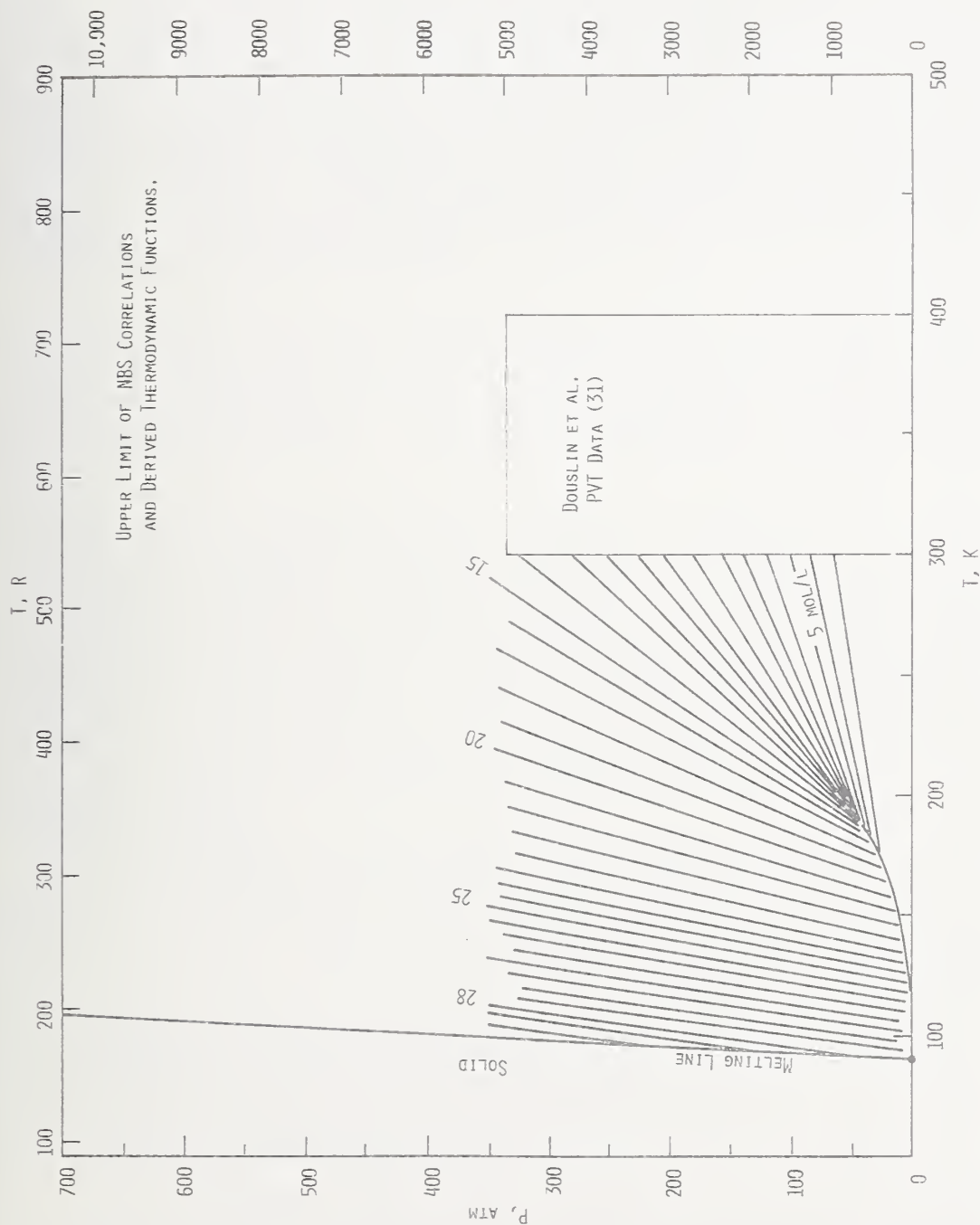


Figure 6. The locus of NBS P-V-T data on isoclores is shown by solid lines. Extrapolation by Goodwin [20] to the limits of NBS correlations are confirmed with limited available data.

Current work in the long term LNG properties program is directed to the second most important constituent of LNG -- ethane. It is the intention of the program to methodically consider each of the pure constituents of LNG in a similar manner as previously described for methane. Current status of the ethane work involves establishing a firm foundation for computing tables of provisional values of thermodynamic functions. The activity has two purposes: to indicate those physical properties for which experimental data are lacking or inadequate and to provide useful results at an early date. These properties include vapor pressure, virial state equation, orthobaric densities, and formulations of the melting line of the ideal gas thermofunctions. Under the present level of effort the work on ethane should be completed in April 1975; propane, the butane and LNG mixtures will follow with a completion date for the entire program by 1980.

Measurements of the liquid vapor equilibria of cryogenic fluids [22], refractive index of liquid and vapor methane and direct measurement of sound velocity and thermal diffusivity are well underway. A program on transport properties -- viscosity, thermal conductivity -- is in the initial state of development.

Reference data on thermal and mechanical properties of structural and insulation materials are essential to facilitate material selection on the basis of cost and safety. Proper material choice is of major economic importance for cryogenic containers, particularly in sea transport of LNG. Studies to define fracture toughness and fatigue crack growth rate in the temperature range 76-300 K are currently being conducted on a series of iron-nickel alloys and aluminum alloys. This materials properties assessment has included the compilation of all the fatigue and fracture data on iron-nickel steels and their weldments; a collection of ship design data and analysis of materials and use; an assessment of the current materials requirements for LNG containers by the American Bureau of Shipping, the U. S. Coast Guard and ASME Pressure Vessel Code. In addition, a bibliography of literature containing data on aluminum alloys, non-metallics and insulation materials is in progress. Results and data for this program should be available after 1 July 1974.

#### Measurement Science and Methodology

Instrumentation and instrumentation methods are essential to process control, safety and custody transfer of liquefied natural gas. The NBS LNG program contains two examples of application of field type measurements. The objective is to define the ability of the instrument to determine and maintain a known accuracy and precision of the parameter of interest, such as density or flow rate.

A density reference system consists of a volume of LNG of adequate size and dimension to accept the measurement element of candidate densitometers. This volume will be filled with LNG of known density traceable to the

reference data established under the mixtures program referred to in the previous section. Density, pressure, temperature and constituent fraction will be varied over a range of controlled conditions and the performance of the densitometer will be evaluated. Long term stability of calibration will be of interest as a logical extension of this work would be the development of a transfer standard for field type densitometer certification. The LNG density reference system is currently in the second year of a three year planned program. The reference system is under construction and proving, with the completion date of the program scheduled for 1975.

The demonstration of an instrumentation method which would measure the heating value of liquefied natural gas flowing in a pipeline is the subject of the second example of measurement science in our LNG program. The project approach combines existing and evolving measurement technology with industry standard practices. The experience gained on a previous cryogenic flowmetering program [23-26] will provide necessary scaling information for the flowmetering portion of this three element measurement system. The second element of the heating value measurement system is a densitometer evaluated and calibrated as described previously. The third element of the heating value measurement involves an industry compatible flow calorimeter which will provide heating value per unit mass. A combination of these three measurement elements should provide a time-based rate for heating value of liquefied natural gas flowing in a pipeline. The objective of this three-year program will be to demonstrate the precision and accuracy of such a measurement system and to provide necessary supportive data for scaling to large pipe sizes. The program is scheduled for completion in 1976.

#### Technology Transfer

It is the objective of this portion of the LNG program to provide a broad dissemination of information on general cryogenic subjects. An LNG Quarterly [27] is published and distributed each April, July, October and January listing all significant papers, reports, and patents relating to LNG, LNG properties and technology. LNG related information has been entered into the NBS Cryogenic Data Center's information system for quick retrieval and comprehensive bibliographies on the properties and technology of LNG are available. There are presently three bibliographies involved; methane properties, methane mixture properties and processes and equipment involving methane and LNG. These three are updated each October [28-30].

A second example of technology transfer is a program concerned with safety of large LNG storage tanks. This program is primarily a consultation and advisory type service to a regulatory agency charged with the responsibility of approval for the location and safe operation of such storage containers.

These examples are of a short term transitory type but indicate the approach in providing this type of information where it is needed and where NBS can provide a proven capability.



## FUTURE PLANS

The ongoing program of providing reference data, measurement science methodology and technology transfer can be projected into the early 1980's. An outline of such research topics is suggested by Table 2. The definition of priorities for these secondary tasks will certainly provide the framework for LNG research in the period 1980-1990 and beyond.

In the long-range future, there may be a number of possibilities for pipeline distribution of energy or development of new sources of energy that will impinge upon gas utility operations, and require continuing definition of research objectives and goals. Several of these possibilities are listed below.

|                                             |                                       |
|---------------------------------------------|---------------------------------------|
| Methanol, distributed as<br>vapor or liquid | Clathrates, hydrates,<br>and hydrides |
| Low-btu gas                                 | Hydrogen                              |
| Coal slurries                               | Ammonia-hydrazine                     |
| Solar energy supplementation                | Geothermal energy                     |

Many of these opportunities will require new facilities and new concepts of business strategy by the gas utilities, but offer important opportunities either on a general basis or in specific localities. A research planning system to monitor and review these alternatives will be the most effective way for the gas utilities to understand and posture themselves to capitalize upon these shifts in a timely fashion.



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## APPENDIX P



# LOW TEMPERATURE FRACTURE BEHAVIOR OF FERRITIC Fe-Ni ALLOY STEELS \*

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Fracture toughness tests over the interval 298-4K and fatigue crack growth rate tests at 298, 111, and 76K are reported on selected Fe-Ni alloys which are commercially available for potential use in storage or transportation of LNG. These alloys include Fe-6Ni and Fe-5Ni in the QLT or austenitized, temperized, and reversion annealed condition, and Fe-9Ni in the quenched and tempered condition. Linear elastic fracture mechanics parameters ( $K_Q$ ,  $K_{IC}$ ) and J-integral ( $J_{IC}$ ) test data are presented for 1.25 inch thick compact tensile specimens. Discussion includes comparisons of fatigue crack growth rate and fracture data between alloys.

Key words: Crack propagation, cryogenics, fracture toughness, iron alloys, mechanical properties, nickel alloys, steels.

\*This work was conducted at the National Bureau of Standards under the sponsorship of the Maritime Administration, U. S. Department of Commerce.

## INTRODUCTION

The increasing role of natural gas as a source of energy has prompted recent research into the mechanical and physical properties of materials related to LNG technology. Considerable effort has been devoted to characterizing the mechanical behavior of materials for use in LNG storage and transportation. The basic design considerations for tankage materials are low temperature strength, fracture toughness, and fatigue properties. Recent research has concentrated on providing such design data for 5083 aluminum alloy and the ferritic 5, 6, and 9Ni steels.

The most important characteristic of the low temperature mechanical behavior of ferritic steels is the ductile-to-brittle transition. The transition occurs over a narrow temperature interval and is marked by an abrupt change in the fracture behavior of sharply notched or cracked specimens. At higher temperatures these materials are ductile and fail by fibrous or dimpled rupture. At temperatures below the transition regime, failure occurs predominantly by cleavage, a brittle fracture mode.

To reduce the probability of brittle fracture in service, the structural applications of ferritic materials are limited to environments where the service temperatures remain above the ductile to brittle transition temperature. A mild steel may be brittle at temperatures near the ice point but, for similarly heat treated steels, the transition can be lowered progressively by increasing nickel concentration<sup>1, 2</sup>

Nine percent nickel steel is a weldable ferritic material which was developed in the 1940's for cryogenic applications<sup>1, 3</sup>. Because it has relatively high strength and retains toughness down to liquid nitrogen temperatures (77 K, -320 °F), it has been used extensively for LNG containment (111 K, 260 °F). Nickel is an expensive alloying element, however, and for economic reasons it has become desirable to optimize the nickel content of ferritic steels intended for LNG tankage.

Five and 6 percent nickel steels were recently developed having reduced nickel concentration while retaining high toughness at 111 K. In these steels the effect of decreased nickel is compensated by the application of a special three step heat treatment. The heat treatment of 5 percent Ni steel has been termed the austenitized, temperized, and reversion annealed condition<sup>4</sup>. The heat treatment of 6 percent Ni steel has been referred to as the QLT condition<sup>2</sup>. Such treatments are departures from the double normalized and tempered or quenched and tempered heat treatments which are applied to 9 percent nickel steel. The details and benefits of the three step heat treatment are described elsewhere<sup>4, 5</sup>

The high toughness levels achieved with nickel steels have created difficulties in measuring valid fracture toughness design data. The transition temperatures are easy to determine by a number of mechanical tests<sup>6</sup>, including Charpy impact; but these tests do not provide data on allowable stress levels for materials in service. Linear elastic fracture mechanics tests are capable of providing a useful design parameter,  $K_{IC}$ ; but  $K_{IC}$  testing of nickel steels has

not proven very successful because large and impractical specimen sizes are required for valid test results.

The recently developed J-integral technique is an important tool for evaluating tough materials such as the nickel steels. The theory of the J-integral was originated by Rice.<sup>7</sup> Subsequent experiments by Begley and Landes<sup>8-10</sup> verified that J can be used as a fracture criterion in cases where the specimen exhibits elastic, elastic-plastic, or fully plastic load-deflection behavior.

A practical consideration is that the specimen size required for J-integral testing is not as large as that for linear elastic  $K_{IC}$  testing. A tentative size criterion for the J-integral test is that<sup>10</sup>:

$$B, b, a \geq 25 (J/\sigma_{\text{flow}})$$

where B is specimen thickness, b is ligament length, a is crack length, and  $\sigma_{\text{flow}}$  is the average value of the 0.2 percent offset yield stress and the ultimate flow stress. B is typically an order of magnitude smaller than the value required for linear elastic behavior as calculated from the size criterion of the ASTM Test for Plan Strain Fracture Toughness of Metallic Materials (E-399-72):

$$B, a \geq 2.5 \left( \frac{K_{IC}}{\sigma_{ys}} \right)^2$$

This paper describes fatigue crack growth rate and fracture toughness tests on 5, 6, and 9 percent Ni steels. J-integral tests are applied to these materials and the fracture parameter  $J_{IC}$  is reported over a wide range of temperatures.  $J_{IC}$  measurements are converted to  $K_{IC}$  values, thus providing useful design data at LNG temperatures and other temperatures of interest.

## EXPERIMENTAL PROCEDURES AND APPARATUS

### Materials

Five, 6 and 9 percent nickel steels were obtained in the form of 1.25 inch thick plates. All materials were commercially heat treated. The 5 percent Ni steel was austenitized, tempered and reversion annealed according to the ASTM Specification for Pressure Vessels Plates, Five Percent Nickel Alloy Steel, Specially Heat Treated (A - 645 - 72a). The 9 percent nickel steel was quenched and tempered according to the ASTM Specification for Pressure Vessel Plates, Alloy Steel, Quenched and Tempered 8 and 9 Percent Nickel (A 553-72a). The 6%Ni steel was in the QLT condition<sup>2</sup>; at present, there is no specification on the heat treatment of this material.

Chemical compositions and mechanical property data are presented in Tables 1 and 2. All tensile properties referred to in this investigation were the average values of two tests performed in accordance with the ASTM Methods of Tension Testing of Metallic Materials (E 8-69).

All fatigue and fracture experiments were performed on 1.25 inch (3.17 cm) thick compact tensile specimens having the geometry illustrated in Figure 1. The width of thickness ratio (W/B) was 2.4, and the planar dimensions were equal to those of a 1.50 inch (3.81 cm) thick specimen proportioned according to ASTM E-399-72. The notch was machined parallel to the rolling direction,



producing a TL orientation. Loadline displacement was measured by means of a modified notch configuration as shown in Figure 1. Roberts' K calibration was used<sup>11</sup>.

### Test Procedures

The majority of tests were conducted at 298 K (70°F), 195 K (-108°F), 111 K (-260°F) and 76 K (-320°F). Two fracture tests were performed in liquid helium at 4 K (-459°F). The temperature of 76 K was obtained by immersion in liquid nitrogen; 195 K was obtained by immersion in a mixture of alcohol and dry ice; and 111 K was obtained by testing in nitrogen vapor. Before testing specimens were allowed between thirty and sixty minutes to reach thermal equilibrium.

A temperature control system with a chromel-constantan thermocouple sensor was used to maintain a temperature of 111 K  $\pm$  3K. The control thermocouple was located on the specimen at the level of the fatigue crack. Vapor from a pressurized liquid nitrogen dewar was introduced to the cryostat through a solenoid valve. The solenoid valve permitted the flow of cold vapor as required by opening and closing automatically in response to the electrical signal from a commercial temperature recorder.

Fatigue testing was conducted on a 20,000 lbs. (100 kN) capacity MTS servo-hydraulic mechanical test system\*. This was a "cryogenic" model

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\*Tradenames of equipment and materials are used for clarity and to conform with standard usage in the literature. Their use does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment or materials are necessarily the best available for the purpose.

with the accuator positioned above the level of the specimen to accommodate the cryostat and to allow access from below for assembling dewars. The testing machine and associated equipment are illustrated in Figure 2.

A 20,000 lb. (100 kN) cryostat was used for fatigue tests. The load carrying frame consists of two tubular stand-off compression members linked at the lower ends with a maraging steel bridge. Fiberglass reinforced plastic was used in construction of the stand-off columns to minimize heat conduction. The lower specimen grip was pinned in place in the center of the bridge, and the upper grip was threaded to the end of the pull rod. A cylindrical fiberglass reinforced plastic dewar was used to enclose the load frame, specimen, and clip gage for cryogenic tests. A similar cryostat was employed in fracture testing, except that the stand-off columns were stainless steel and load carrying capacity was 60,000 lbs. (267 MN).

ASTM type clip gages were used at all testing temperatures. Commercially available foil resistance strain gage films were bonded to the clip gage beams using an adhesive suitable for low temperature applications. The clip gages were calibrated at temperatures from 298 K to 76 K, but there was not a large change in sensitivity. Clip gage linearity met the requirements of ASTM E-399-72 over the maximum operating range of up to 0.090 inches (0.229 cm) displacement.

#### Crack Growth Rate Tests

Fatigue tests were performed using load control at a frequency of 24 Hz. The load cycle was sinusoidal at a constant stress ratio (minimum/maximum load) of 0.1. Dynamic fatigue loads were measured and controlled to within 1-2 percent by means of a digital peak recording device.

The change in crack length during crack growth rate tests was monitored by compliance measurements. Direct measurement of crack lengths at the specimen surface was not possible during cryogenic tests. The compliance technique is based on the fact that for a given load, the specimen compliance (reciprocal of stiffness) increases with increasing crack length. Compliance methods are discussed in detail elsewhere<sup>12,13</sup>.

Experimental crack length-compliance correlations were obtained for each material and temperature. An X-Y recorder was used to measure the compliance for a number of specimens of varying crack lengths. Fatigue striations were generated by load changes during precracking and crack growth rate tests so that several crack length-compliance measurements were obtained from each specimen. The data were plotted as a function of crack length which was measured as an average of three readings at the center and quarter points of specimen thickness.

Theoretical crack length-compliance curves were calculated from the generalized solution given by Roberts<sup>11</sup> but these were not in complete agreement with the experimental correlations. Comparison showed that the calculated curves consistently under estimated the true crack lengths by 2-4%. The difference between the calculated and the experimental curves may result from crack front curvature effects, but it can not be attributed to uncertainty in calculations since Young's moduli were known to within 1% at all temperatures from tests on the same stock materials<sup>14</sup>.

The procedure for determining crack growth rates involved plotting the static compliance at intervals during the tests. Using the experimental crack length - compliance correlation, crack length could then be obtained,

to within  $\pm 1.5$  percent. Crack length (a) was plotted versus the total number (N) of fatigue cycles and the crack growth rate (da/dN) was determined by graphical differentiation of the a vs. N curve.

It is well known that the rate of crack growth may be retarded by changing from a higher to a lower stress intensity range. Crack growth rates may also be influenced by abrupt temperature changes. Whenever these kinds of changes were made the crack growth rate was allowed to stabilize before data were accepted as valid. Crack growth data under the new conditions were ignored until the crack had advanced an increment equal to or greater than the plastic zone size as calculated from Irwin's formula<sup>15</sup>.

#### Fracture Toughness Tests

Fracture tests were conducted using a 60,000 lb. (267 kN) capacity hydraulic testing machine. The loading rate was constant, corresponding to a crosshead displacement of  $0.02 \text{ in min}^{-1}$  ( $8.5 \times 10^{-4} \text{ cm} \cdot \text{sec}^{-1}$ ).

Most specimens were precracked at the temperature of subsequent fracture testing; the few exceptions are noted in the text. The final crack length was deep, corresponding to a ratio a/W of between 0.60 and 0.62. Precracking was performed at fatigue loads always less than half of the specimen limit load and at stress intensities never exceeding a value of  $0.002 \text{ in}^{1/2} \times \text{Young's modulus}$ .  $K_Q$  was measured according to the method described in E-399, using the same J-integral test specimens.

For the deeply cracked compact tensile specimens described in this report, J was calculated from the equation<sup>16,10</sup>:

$$J = \frac{2A}{Bb}$$

where A is the area under the load deflection curve to a particular value

of displacement. The critical value  $J_{IC}$  is the value of  $J$  just prior to crack extension. For specimens which exhibited unstable crack extension (pop-in),  $J_{IC}$  was calculated using the load at the first pop-in. When crack extension took place by stable ductile tearing the  $J_{IC}$  value was obtained by extrapolation of the  $J$  versus crack extension curve.

The extrapolation technique was based on a method outlined by Landes and Begley<sup>10</sup>. According to the procedure, 3-5 nearly identical specimens with average crack lengths agreeing to approximately 3 percent were tested at each temperature. A series of load-deflection curves were obtained by loading each specimen to a level sufficient to cause decreasing amounts of crack extension. The specimens were then unloaded and heat tinted 20 minutes at 538 K (1000 °F) to oxidize the surfaces where crack extension had taken place. The samples were subsequently pulled apart at 298 K. The average value of  $\Delta a$  was measured and plotted versus the corresponding value of  $J$ .

It was observed in these tests that deformation at the crack tip preceded material separation. Apparent crack extension therefore included a contribution due to deformation in addition to actual material separation. The deformation was visible on the fractured samples as a zone between the fatigue cracked region and the torn ligament. The material in the stretch zone had been deformed out of the plane of the fatigue crack surface.

The length of the stretch zone was measured with a traveling microscope. An average value of several measurements from each specimen was



plotted as a vertical line on the J vs.  $\Delta a$  graphs. The intersection of the J vs.  $\Delta a$  curve with the stretch zone line was taken to represent the initial point of material separation, and  $J_{IC}$  was obtained as the value of J at the point of intersection.

Landes and Begley<sup>10</sup> recommend construction of the  $J/2\sigma_{flow}$  line to establish the J resistance curve over the stretch zone interval.

For 9% Ni steel, construction of the  $J/2\sigma_{flow}$  line resulted in a triple intersection with the vertical stretch zone line and the J vs.  $\Delta a$  curve. For the other materials, the  $J/2\sigma_{flow}$  line intersection point was less compatible with the data. In some cases, material separation was observed at values of  $\Delta a$  less than those predicted by the  $J/2\sigma_{flow}$  intersection point and it appeared that a  $J/3\sigma_{flow}$  line would have resulted in better agreement. The intersection point defined by the vertical stretch zone line was chosen for consistency. The attempt to measure the extension of the stretch zone directly is a technique which may not be generally applicable; it depends on the ease of identifying the stretch zone visually.

When the J versus  $\Delta a$  graphs appeared to be linear,  $J_{IC}$  was determined by a "best" straight line extrapolation. In other cases a linear trend was not clearly defined. Scatter in the data was accounted for by examining a number of reasonable extrapolations and a range of possible  $J_{IC}$  values were determined.

$K_{IC}$  values were calculated from the  $J_{IC}$  measurements according to the relation<sup>8, 9</sup>:

$$K_{IC} = (J_{IC} \cdot \frac{E}{1-\nu^2})^{1/2}$$

where E is Young's modulus and  $\nu$  is Poisson's ratio. Data on the elastic constants at all temperatures were available from the work of Weston et al.<sup>14</sup>

## RESULTS

### Fatigue Crack Growth Rate

Figures 3 - 5 summarize the fatigue crack growth rate results for all three materials. The data conform to the relation<sup>17</sup>

$$da/dN = C(\Delta K)^n$$

where  $da/dN$  is the change in crack length per cycle,  $\Delta K$  is the range of stress intensity and C and n are empirical constants.

Figure 3 illustrates that the crack growth rate behavior of 5 percent Ni steel appears to be temperature independent for stress intensity ranges from 20-25 ksi  $\cdot$  in<sup>1/2</sup> (22 - 27 MNm<sup>-22</sup>  $\cdot$  m<sup>1/2</sup>). Above  $\Delta K =$  ksi  $\cdot$  in<sup>1/2</sup> (33 MNm<sup>-2</sup>  $\cdot$  m<sup>1/2</sup>) growth rates at 76 K are definitely higher than at room temperature or 111 K.

Superimposed on the data of Figure 3 are straight line approximations of the data reported by Bucci, et al.<sup>18</sup>. The straight line approximations are used for clarity in illustrating data trends, but do not indicate the degree of scatter in their results. The present results are in good agreement with the data from this source.

Fatigue crack growth rate data for 6 percent and 9 percent Ni steel followed the same trend observed for 5 percent Ni steel. As shown in Figures 4 and 5, the crack growth rates were somewhat higher at 76 K than at 298 K for stress intensity ranges above 25 ksi  $\cdot$  in<sup>1/2</sup> (27.5 MNm<sup>-2</sup>  $\cdot$  m<sup>1/2</sup>).

Figure 4 shows that the crack growth rate results for 6 percent Ni steel at 111 K agreed well with room temperature data over the entire range of  $\Delta K$ . The increase in growth rates occurred between 111 and 76 K. This effect may be related to the fact that 6 percent Ni alloy begins its ductile-to-brittle transition near liquid nitrogen temperatures. There is no published data in the literature with which to compare the present results for 6 percent Ni steel.

The results of Bucci, et al.<sup>18</sup> for 9 percent Ni steel are represented in Figure 5. The present results reveal a somewhat higher growth rate at 76 K, but the general agreement is good.

The fatigue crack growth rate behavior of 5, 6, and 9 percent Ni steels appears to be similar. If all data from this report are superimposed on a single graph, it appears that the fatigue crack growth rates of the three materials are nearly equivalent for  $\Delta K$  values ranging from 20 - 60 ksi  $\cdot$  in<sup>1/2</sup> (22 - 66 Nm<sup>-2</sup>  $\cdot$  m<sup>1/2</sup>).

#### Fracture Toughness

Representative load-deflection curves for 5 percent Ni steel are illustrated in Figure 6. The arrows terminating the curves at 298 K and 195 K indicate that ductile tearing continued to larger deflections without the occurrence of pop-in. At 111 K an appreciable amount of plastic deformation occurred, followed by a single pop-in. Multiple pop-ins occurred at temperatures below 111 K where linear elastic behavior was approached. At 76 K, the load continued to increase significantly after the first pop-in. The deviation from linearity at the upper end of the 4 K load-deflection curve was due to a series of faint but audible pop-ins.

The load-deflection curves for 6 percent and 9 percent Ni steels are illustrated in Figures 7 and 8. In comparison, it is significant to note that pop-in did not occur in tests of 6 percent Ni at 111 K.

The fracture surfaces of 6 percent and 9 percent Ni steel specimens exhibited 40 - 50 percent slant fracture at 298 K. Shear lips took the form of high cusps rising 0.4 inch (1 cm) above the plane of the fatigue crack. There was also a large lateral contraction in the thickness direction, amounting to 12 percent. As temperature decreased to 76 K, the proportion of slant fracture decreased to about 15 percent, and the percentage of lateral contraction decreased to approximately 5 percent.

For 5 percent Ni steel, a lateral contraction of 18 percent was measured at room temperature, but the fracture surface was relatively flat compared to the other materials. The proportion of slant fracture decreased from about 25 percent at room temperature to zero at 5 K. At 4 K the fracture surface exhibited reflective cleavage facets.

For 6 percent and 9 percent Ni steels the degree of crack front curvature bordered on, but did not exceed, the limits established for fatigue crack uniformity (ASTM E-399-72). In the case of 5 percent Ni steel crack front straightness requirements were occasionally violated when the crack length at the specimen edge was found to be less than 90 percent of the average crack length. The difference in edge crack and average crack lengths ranged from 87-88 percent for the four specimens which did not meet this requirement. The degree of crack front curvature appears to depend on loading history. Crack growth rate specimens tested at higher stress intensities had less curvature; the specimens with excessive curvature

were those used in low temperature fracture tests where the maximum stress intensities ( $K_f$ ) were lowered to comply with the  $K_f \leq .6K_Q$  criterion of ASTM E-399-72.

Graphs of  $J$  versus  $\Delta a$  are shown in Figures 9-11. Tabulations of the data used in determining the parameters  $J_{IC}$ ,  $K_{IC}$  and  $K_Q$  are presented in Tables 3-8, and Table 9 presents an evaluation of the size criteria for valid testing.

The results are summarized in Figure 12, which illustrates the temperature dependence of the parameters  $K_Q$  and  $K_{IC}$ . For all three materials,  $K_Q$  increased with decreasing temperature over the interval 298 K - 76 K. At these temperatures  $K_Q$  does not represent a valid fracture parameter for 1.25 inch thick specimens - the ASTM E-399-72 thickness requirement is not satisfied. The  $K_Q$  values measured under non-linear elastic conditions have no practical significance and are included merely for comparison. Over the interval 298-76 K, it was observed that:

1. The disagreement between  $K_Q$  and  $K_{IC}$  values was largest at ambient temperatures;
2. The effect of temperature on  $K_Q$  was opposite to the general trend displayed by  $K_{IC}$  values; and
3. The  $K_Q$  values did not provide an indication of the relative toughness of the materials. For example, 9 percent Ni steel exhibited the highest  $K_Q$  values but not the highest  $K_{IC}$  values.



Only in tests of 5 percent Ni steel at 76 K and 4 K did the  $K_Q$  values agree with the  $K_{IC}$  values converted from J-integral measurements. Nevertheless, these  $K_Q$  values did not qualify as valid  $K_{IC}$  according to ASTM E-299-72. This point is amplified in the discussion.

For 5 percent Ni steel,  $K_{IC}$  values decreased from  $200 \text{ ksi} \cdot \text{in}^{1/2}$  ( $220 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) at room temperature to  $50 \text{ ksi} \cdot \text{in}^{1/2}$  ( $55 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) at 4 K. The datum point at 195 K was determined by extrapolation of only two fracture tests and should not be heavily weighted. The fracture toughness remained nearly equivalent to that of 9 percent Ni steel at temperatures as low as 111 K. Below 111 K the  $K_{IC}$  values decreased abruptly.

The 9 percent Ni steel was tested at 298 K and 76 K.  $K_{IC}$  decreased from  $210 \text{ ksi} \cdot \text{in}^{1/2}$  ( $230 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) at 298 K to  $167 \text{ ksi} \cdot \text{in}^{1/2}$  ( $184 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) at 76 K, a reduction of 15 percent. A more drastic reduction in toughness over this temperature interval was not expected. Charpy impact data from the mill analysis of this material indicate that the ductile-to-brittle transition is just beginning at 76 K. Additional testing at temperatures lower than 76 K would be necessary to define the ductile-to-brittle transition temperature regime in terms of  $K_{IC}$  values.

The fracture toughness of the 6 percent Ni alloy exceeded that of the other materials tested.  $K_{IC}$  values indicated that the upper shelf toughness tended to increase from about  $240 \text{ ksi} \cdot \text{in}^{1/2}$  ( $263 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) to  $268 \text{ ksi} \cdot \text{in}^{1/2}$  ( $294 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) over the interval 298 - 111 K. However, a rather sharp drop in the data occurs between 111 and 76 K,

indicating the beginning of the ductile-to-brittle transition. The value of  $K_{IC}$  declined to  $195 \text{ ksi} \cdot \text{in}^{1/2}$  ( $214 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ), slightly higher than the value obtained for 9 percent Ni steel.

It was observed in a few tests on 6 percent Ni steel that a small amount of stable crack extension preceded pop-in at 76 K. For testing convenience, this effect was neglected and  $J_{IC}$  values were calculated at the point of pop-in. A rigorously determined  $J_{IC}$  measurement would be slightly lower than the value calculated at pop-in; but the error introduced in  $K_{IC}$  determinations was estimated to be less than 5 percent which is less than the degree of scatter observed in replicate tests. It is probable that some amount of stable crack extension preceded pop-in tests of 5 percent Ni steel at 111 K, but observations were inconclusive.

## DISCUSSION

Previous authors<sup>19-23</sup> have not reported valid  $K_{IC}$  data for 5, 6, or 9 percent nickel base metal steels. The J-integral test procedures used in this investigation appeared to provide valid  $K_{IC}$  data. Several factors must be considered in assessing the validity of the present results.

The J-integral test results indicated ambient temperature  $K_{IC}$  values as high as  $200\text{-}240 \text{ ksi} \cdot \text{in}^{1/2}$  ( $220\text{-}263 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ). These values are quite reasonable. The size criterion was satisfied at all temperatures. Confidence in the data stems from the fact that this size criterion was established from tests on steels<sup>8-10</sup> equivalent in fracture toughness ( $J_{IC} = 1000\text{-}2000 \text{ in} \cdot \text{lb} \cdot \text{in}^{-2}$  or  $0.175 - 0.350 \text{ MJ} \cdot \text{m}^{-2}$ ) to the nickel steels tested in this report.

Serious problems regarding test validity arose only in tests of 5 percent Ni steel at 76 K and 4 K. At 4 K the linear elastic size criterion was satisfied but precracking stress intensities could not be lowered successfully to comply with the criterion that  $K_f \leq .6 K_Q$ . At 4 K the  $K_Q$  was relatively low and crack front curvature increased significantly at the lower fatigue stress intensities. To keep the crack front curvature within reasonable limits, one specimen was precracked at 298 K ( $K_f \leq 0.6 K_Q$ ) and a second specimen was precracked at 76 K ( $K_f \leq .75 K_Q$ ). The first specimen satisfied crack front curvature requirements but  $K_Q$  was  $10 \text{ ksi} \cdot \text{in}^{1/2}$  higher than the specimen precracked at 76 K. It is probable that precracking at 298 K introduced disparities in plastic zone size and crack sharpness. The specimen precracked at 76 K fell 2 percent short of the requirement that the edge crack length be 90% or more of the average crack length. For this specimen, the measured value of  $50 \text{ ksi} \cdot \text{in}^{1/2}$  is probably closer to the true value of fracture toughness; however, neither of the tests at 4 K can be considered valid.

For 5 percent Ni steel at 76 K, the ASTM Method E-399-72 requires a specimen thickness of 1.5 - 1.6 inches ( $\approx 4 \text{ cm}$ ). In two tests at 76 K,  $K_f$  was maintained  $< 0.6 K_Q$  but the edge crack lengths were 87-88 percent of the average crack lengths; 90 percent or more is required. Therefore the  $K_Q$  data are invalid according to a strict interpretation of ASTM E-399-82. On the other hand, the size criterion for J-integral testing is amply satisfied. The magnitude of the effect of a minor transgression in crack front curvature is not known, but it appears that there could be only a small error in the data for 5 percent Ni steel at 76 K.

Agreement of  $K_Q$  values with  $K_{IC}$  values converted from  $J_{IC}$  measurements implies that the linear elastic fracture mechanics test is valid from the standpoint of size considerations. J-integral results can then be used to evaluate the linear elastic thickness requirement. For 5 percent Ni steel at 76 K, the mean value of  $K_{IC}$  was  $87 \text{ ksi} \cdot \text{in}^{1/2}$  ( $95 \text{ MNm}^{-2} \cdot \text{m}^{1/2}$ ) and the 0.2 percent offset yield strength was  $\sim 110 \text{ ksi}$  ( $76 \text{ Nm}^{-2}$ ). These data suggest that the ASTM size criterion factor of 2.5 is slightly conservative in the case of 5 percent Ni steel. The factor could be reduced to 2.0, since a calculation shows that:

$$B = 1.25 \text{ inch} \cong 2.0 \left( \frac{K_{IC}^2}{\sigma_{ys}^2} \right)_{76 \text{ K}}.$$

The 6 percent Ni steel contained low levels of sulfur and phosphorous, a relatively high percentage of manganese, and some chrome (Table 1). Sulfur and phosphorous are tramp elements, usually deleterious in their effects on mechanical properties, whereas manganese is beneficial with respect to microstructural refinement<sup>2</sup>. Thus, compositional variations may account for the somewhat higher fracture toughness observed for 6 percent Ni steel.

The present results confirm that 5 percent and 6 percent Ni steels are promising materials for potential use in LNG tankage applications. At 111 K, the fracture properties of these newly developed steels are comparable to those of 9 percent Ni steel. Further evaluation is needed to determine the properties of weldments and their heat affected zones (HAZ). It is probable that the fracture toughness of these materials will be lowered somewhat by the deleterious effects of heat inputs from welding. Therefore, the ultimate

suitability of 5 percent and 6 percent Ni steels must be determined by fracture toughness comparisons of both the base metals, the weld, and the HAZ.

#### SUMMARY

1. The fatigue crack growth rates of 5, 6, and 9 percent Ni steels were nearly equivalent at  $\Delta K$  from 20-60 ksi  $\cdot$  in<sup>1/2</sup> (22-66 MNm<sup>-2</sup>  $\cdot$  m<sup>1/2</sup>).
2. At  $\Delta K > 25$  ksi  $\cdot$  in<sup>1/2</sup> (27.6 MNm<sup>-2</sup>) the fatigue crack growth rates of 5 and 6 Ni steels were higher at 76 K than at 111 K or 298 K.
3. The J- integral test procedures used in this investigation appeared to yield valid  $K_{IC}$  data for the 5, 6, and 9 Ni steels.
4. For 9 Ni steel there was only a small decrease in fracture toughness over the interval 298 - 76 K; the fracture toughness of 5 and 6 Ni steels decreased abruptly over the interval 111 - 76 K.
5. At 111 K, the fracture toughness of these materials ranged from 160 ksi  $\cdot$  in<sup>1/2</sup> to 270 ksi  $\cdot$  in<sup>1/2</sup> (180 - 300 MNm<sup>-2</sup>  $\cdot$  m<sup>1/2</sup>).

#### ACKNOWLEDGMENTS

The authors would like to thank Steve Keefer who assisted in data reduction.



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Table 1. Chemical Composition

| Alloy  | Mill Analyses (wt. pct.) |      |      |       |       |       |      |      |       |       |       |
|--------|--------------------------|------|------|-------|-------|-------|------|------|-------|-------|-------|
|        | Fe                       | C    | Mn   | P     | S     | Si    | Ni   | Cr   | Mo    | Al    | N     |
| Fe-5Ni | Bal                      | 0.13 | 0.45 | 0.025 | 0.025 | 0.275 | 5.00 | -    | 0.275 | 0.085 | 0.020 |
| Fe-6Ni | Bal                      | 0.06 | 1.12 | 0.005 | 0.004 | 0.24  | 5.66 | 0.63 | 0.18  | -     | -     |
| Fe-9Ni | Bal                      | 0.06 | 0.56 | 0.007 | 0.003 | 0.27  | 9.25 | -    | -     | -     | -     |

Table 2. Mechanical Properties

|          | 0.2% Offset<br>Yield Strength<br>(ksi) | Tensile<br>Strength<br>(ksi) | Elongation<br>(%) | Reduction<br>of Area<br>(%) | Hardness<br>(Rc) | C <sub>v</sub> (longitudinal)<br>76 K (ft·lbs) |
|----------|----------------------------------------|------------------------------|-------------------|-----------------------------|------------------|------------------------------------------------|
| Fe-5% Ni | 77.5                                   | 97.9                         | 34                | 79                          | 20               | 38                                             |
| Fe-6% Ni | 82.0                                   | 106.6                        | 30                | 81                          | 23               | 166                                            |
| Fe-9% Ni | 99.9                                   | 109.1                        | 27                | 78                          | 25               | 130                                            |

NOTE: 1 ksi = 0.689 Nm<sup>-2</sup>.

| Temp<br>(K) | Spec <sup>*</sup> | $\frac{a}{W}$ | $P_Q$<br>(lb) | $K_Q$<br>(ksi $\sqrt{\text{in}}$ ) |
|-------------|-------------------|---------------|---------------|------------------------------------|
| 298         | 16                | 0.597         | 10,200        | 62                                 |
| 298         | 3                 | 0.60          | 9,150         | 56.4                               |
| 298         | 11                | 0.60          | 9,900         | 60.8                               |
| 298         | A                 | 0.597         | 14,100        | <u>86.8</u>                        |
|             |                   |               | Avg =         | 66.5                               |
| 195         | 21 <sup>†</sup>   | 0.607         | 13,100        | 83.7                               |
| 195         | 22 <sup>†</sup>   | 0.611         | 11,450        | 74.4                               |
| 195         | 23 <sup>†</sup>   | 0.617         | 13,400        | <u>89.5</u>                        |
|             |                   |               | Avg =         | 82.5                               |
| 111         | 24                | 0.621         | 13,400        | 90.7                               |
| 111         | 29                | 0.654         | 11,700        | 92.7                               |
| 111         | 32                | 0.623         | 17,200        | <u>117</u>                         |
|             |                   |               | Avg =         | 100                                |
| 76          | 25                | 0.599         | 12,950        | 82.0                               |
| 76          | 27                | 0.612         | 13,200        | <u>86.1</u>                        |
|             |                   |               | Avg =         | 84.0                               |
| 4           | 28 <sup>†</sup>   | 0.624         | 8,550         | 60.1                               |
| 4           | 26 <sup>††</sup>  | 0.606         | 7,950         | <u>50.2</u>                        |
|             |                   |               | Avg =         | 55.2                               |

Notes:

1 lb = 4.448 N

1 ksi  $\sqrt{\text{in}}$  =  $1.098 \times 10^6 \text{ Nm}^{-2} \sqrt{\text{m}}$

\* B = 1.228 in (3.119 cm)  $\pm$  0.5%,

W = 3.034 in (7.706 cm)  $\pm$  0.9%

† precracked at 298 K

†† precracked at 76 K



Table 4. J-Integral and Converted  $K_{IC}$  of Fe-5% Ni

| Temp<br>(K) | Spec             | b<br>(in) | $J$<br>$\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$ | $\Delta a_{\text{ave}}$<br>(in) | Stretch<br>Zone | $J_{IC}$<br>$\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$ | $K_{IC}$<br>(ksi $\sqrt{\text{in}}$ ) |
|-------------|------------------|-----------|-------------------------------------------------------------|---------------------------------|-----------------|------------------------------------------------------------------|---------------------------------------|
| 298         | 16               | 1.240     | 3.42                                                        | 0.041                           | 0.004           |                                                                  |                                       |
| 298         | 3                | 1.214     | 2.47                                                        | 0.022                           | 0.006           |                                                                  |                                       |
| 298         | 11               | 1.216     | 1.76                                                        | 0.011                           | 0.003           |                                                                  |                                       |
| 298         | A                | 1.204     | 1.34                                                        | 0.010                           | <u>0.004</u>    |                                                                  |                                       |
| Avg =       |                  |           |                                                             |                                 | 0.004           | $1.27 \pm 0.19$                                                  | $200 \pm 15$                          |
| 195         | 21 <sup>†</sup>  | 1.191     | 4.16                                                        | 0.046                           | 0.005           |                                                                  |                                       |
| 195         | 22 <sup>†</sup>  | 1.179     | 2.58                                                        | 0.020                           | <u>0.004</u>    |                                                                  |                                       |
| Avg =       |                  |           |                                                             |                                 | 0.0045          | 1.41                                                             | 210                                   |
| 111         | 24               | 1.146     | N/A                                                         | N/A                             | N/A             | 1.05                                                             | 185                                   |
| 111         | 29               | 1.053     | "                                                           | "                               | "               | 1.09                                                             | 189                                   |
| 111         | 32               | 1.145     | "                                                           | "                               | "               | <u>0.774</u>                                                     | 159                                   |
| Avg =       |                  |           |                                                             |                                 |                 | 0.972                                                            | 178                                   |
| 76          | 25               | 1.217     | "                                                           | "                               | "               | 0.178                                                            | 76.5                                  |
| 76          | 27               | 1.180     | "                                                           | "                               | "               | <u>0.287</u>                                                     | <u>97.1</u>                           |
| Avg =       |                  |           |                                                             |                                 |                 | 0.232                                                            | 86.8                                  |
| 4           | 28 <sup>†</sup>  | 1.138     | "                                                           | "                               | "               | 0.102                                                            | 58                                    |
| 4           | 26 <sup>††</sup> | 1.193     | "                                                           | "                               | "               | <u>0.074</u>                                                     | <u>49.4</u>                           |
| Avg =       |                  |           |                                                             |                                 |                 | 0.088                                                            | 53.7                                  |

Notes: 1 in = 2.54 cm

$$1 \frac{\text{in-lb}}{\text{in}^2} = 1.75 \times 10^2 \text{ Jm}^{-2}$$

$$1 \text{ ksi } \sqrt{\text{in}} = 1.098 \times 10^6 \text{ Nm}^{-2} \sqrt{\text{m}}$$

† precracked at 298 K

†† precracked at 76 K

| Temp<br>(K) | Spec | $\frac{a}{W}$ | $P_Q$<br>(lb) | $K_Q$<br>(ksi $\sqrt{\text{in}}$ ) |
|-------------|------|---------------|---------------|------------------------------------|
| 298         | 7    | 0.614         | 12,500        | 83                                 |
| 298         | 1    | 0.617         | 12,950        | 87                                 |
| 298         | 5    | 0.619         | 13,700        | 92                                 |
| 298         | 3    | 0.620         | 16,300        | 111                                |
| 298         | 2    | 0.615         | 14,950        | 100                                |
| 298         | 15   | 0.615         | 12,950        | <u>84</u>                          |
| Avg =       |      |               |               | 93                                 |
| 195         | 18   | 0.607         | 14,250        | 89                                 |
| 195         | 17   | 0.605         | 13,500        | 83                                 |
| 195         | 16   | 0.591         | 14,500        | 86                                 |
| 195         | 19   | 0.592         | 14,500        | <u>86</u>                          |
| Avg =       |      |               |               | 86                                 |
| 111         | 20   | 0.614         | 17,250        | 114                                |
| 111         | 21   | 0.616         | 18,300        | 117                                |
| 111         | 22   | 0.614         | 18,300        | 120                                |
| 111         | 23   | 0.613         | 16,750        | <u>113</u>                         |
| Avg =       |      |               |               | 116                                |
| 76          | 12   | 0.607         | 20,300        | 128                                |
| 76          | 11   | 0.607         | 18,300        | 115                                |
| 76          | 8    | 0.617         | 19,650        | 130                                |
| 76          | 10   | 0.612         | 21,050        | <u>136</u>                         |
| Avg =       |      |               |               | 127                                |

Notes: 1 lb = 4.448 N

$$1 \text{ ksi } \sqrt{\text{in}} = 1.098 \times 10^6 \text{ Nm}^{-2} \sqrt{\text{m}}$$

$$* B = 1.250 \text{ in (3.178 cm)} \pm 0.4\%,$$

$$W = 3.046 \text{ in (7.737 cm)} \pm 0.6\%.$$

Table 6. J-Integral and Converted  $K_{IC}$  of Fe-6% Ni

| Temp<br>(K) | Spec | b<br>(in) | J<br>$\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$ | $\Delta a_{ave}$<br>(in) | Stretch<br>Zone<br>(in) | $J_{IC}$<br>$\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$ | $K_{IC}$<br>(ksi $\sqrt{\text{in}}$ ) |
|-------------|------|-----------|-----------------------------------------------------------|--------------------------|-------------------------|------------------------------------------------------------------|---------------------------------------|
| 298         | 7    | 1.159     | 6.14                                                      | 0.052                    | 0.006                   |                                                                  |                                       |
| 298         | 1    | 1.167     | 4.57                                                      | 0.033                    | 0.008                   |                                                                  |                                       |
| 298         | 5    | 1.159     | 2.07                                                      | 0.008                    | 0.005                   |                                                                  |                                       |
| 298         | 15   | 1.174     | 2.58                                                      | 0.013                    | <u>0.005</u>            |                                                                  |                                       |
|             |      |           |                                                           | Avg =                    | 0.006                   | $1.75 \pm 0.14$                                                  | $236 \pm 9$                           |
| 195         | 18   | 1.208     | 2.90                                                      | 0.015                    | 0.006                   |                                                                  |                                       |
| 195         | 17   | 1.205     | 6.99                                                      | 0.061                    | 0.007                   |                                                                  |                                       |
| 195         | 16   | 1.247     | 5.18                                                      | 0.034                    | 0.007                   |                                                                  |                                       |
| 195         | 19   | 1.243     | 4.12                                                      | 0.028                    | <u>0.006</u>            |                                                                  |                                       |
|             |      |           |                                                           | Avg =                    | 0.006                   | $2.25 \pm 0.15$                                                  | $272 \pm 9$                           |
| 111         | 20   | 1.172     | 5.86                                                      | 0.040                    | 0.004                   |                                                                  |                                       |
| 111         | 21   | 1.168     | 4.54                                                      | 0.030                    | 0.005                   |                                                                  |                                       |
| 111         | 22   | 1.176     | 2.74                                                      | 0.011                    | 0.005                   |                                                                  |                                       |
| 111         | 23   | 1.177     | 3.65                                                      | 0.018                    | <u>0.006</u>            |                                                                  |                                       |
|             |      |           |                                                           | Avg =                    | 0.005                   | $2.15 \pm 0.13$                                                  | $268 \pm 9$                           |
| 76          | 12   | 1.194     | N/A                                                       | N/A                      |                         | 1.30                                                             | 208                                   |
| 76          | 11   | 1.195     | "                                                         | "                        |                         | 1.30                                                             | 208                                   |
| 76          | 8    | 1.165     | "                                                         | "                        |                         | 0.944                                                            | 177                                   |
| 76          | 10   | 1.180     | "                                                         | "                        |                         | <u>1.14</u>                                                      | 195                                   |
|             |      |           |                                                           | Avg =                    |                         | 1.17                                                             | 197                                   |

Notes: 1 in = 2.54 cm

$$1 \frac{\text{in-lb}}{\text{in}^2} = 1.75 \times 10^2 \text{ Jm}^{-2}$$

$$= 1 \text{ ksi } \sqrt{\text{in}} = 1.098 \times 10^6 \text{ Nm}^{-2} \sqrt{\text{m}}$$

Table 7.  $K_Q$  of Fe-9% Ni

| Temp<br>K | Spec <sup>*</sup> | $\frac{a}{W}$ | $P_Q$<br>(lb) | $K_Q$<br>(ksi $\sqrt{\text{in}}$ ) |
|-----------|-------------------|---------------|---------------|------------------------------------|
| 298       | 6                 | 0.594         | 19,200        | 116                                |
|           | 9                 | 0.606         | 19,200        | 121                                |
|           | 12                | 0.601         | 18,900        | 117                                |
|           | 4                 | 0.599         | 19,050        | 116                                |
|           | 18                | 0.617         | 17,400        | <u>114</u>                         |
|           |                   |               | Avg =         | 117                                |
| 76        | 19                | 0.615         | 21,150        | 137                                |
|           | 20                | 0.609         | 22,700        | 142                                |
|           | 21                | 0.614         | 22,250        | <u>144</u>                         |
|           |                   |               | Avg =         | 141                                |

Notes: 1 lb = 4.448 N

1 ksi  $\sqrt{\text{in}}$  =  $1.098 \times 10^6 \text{ Nm}^{-2} \sqrt{\text{m}}$

\* B = 1.253 in (3.182 cm)  $\pm$  .2%,

W = 3.036 in (7.711 cm)  $\pm$  .5%.

Table 8. J - Integral and Converted  $K_{IC}$  of Fe-9% Ni

| Temp<br>(K) | Spec | b<br>(in) | J<br>$\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$ | $\Delta a_{\text{ave}}$<br>(in) | Stretch<br>Zone<br>(in) | $J_{IC}$<br>$\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$ | $K_{IC}$<br>(ksi $\sqrt{\text{in}}$ ) |
|-------------|------|-----------|-----------------------------------------------------------|---------------------------------|-------------------------|------------------------------------------------------------------|---------------------------------------|
| 298         | 6    | 1.236     | 2.70                                                      | 0.021                           | 0.007                   |                                                                  |                                       |
| 298         | 9    | 1.20      | 4.02                                                      | 0.028                           | 0.007                   |                                                                  |                                       |
| 298         | 12   | 1.213     | 4.92                                                      | 0.044                           | 0.006                   |                                                                  |                                       |
| 298         | 4    | 1.219     | 6.80                                                      | 0.054                           | 0.007                   |                                                                  |                                       |
| 298         | 18   | 1.168     | 1.22                                                      |                                 | 0.007                   |                                                                  |                                       |
|             |      |           |                                                           | Avg =                           | 0.007                   | $1.14 \pm 23$                                                    | $210 \pm 3$                           |
| 76          | 19   | 1.159     | N/A                                                       | N/A                             | N/A                     | 0.810                                                            | 162                                   |
| 76          | 20   | 1.185     | "                                                         | "                               | "                       | 0.935                                                            | 174                                   |
| 76          | 21   | 1.172     | "                                                         | "                               | "                       | 0.846                                                            | 165                                   |
|             |      |           |                                                           |                                 | Avg =                   | 0.864                                                            | 167                                   |

Notes: 1 in = 2.54 cm

$$1 \frac{\text{in-lb}}{\text{in}^2} = 1.75 \times 10^2 \frac{\text{m} \cdot \text{N}}{\text{m}^2} \text{ Jm}^{-2}$$

$$1 \text{ ksi } \sqrt{\text{in}} = 1.098 \times 10^6 \frac{\text{N}}{\text{m}^2} \sqrt{\text{m}} \text{ Nm}^{-2} \sqrt{\text{m}}$$



Table 9. Dimensional Criteria for Valid  $K_{IC}$  and  $J_{IC}$

| Alloy    | Temp<br>(K) | a<br>(in) | B<br>(in) | b<br>(in) | $2.5 \left( \frac{K_Q}{\sigma_{ys}} \right)^2$<br>(in) | $2.5 \left( \frac{K_{IC}^*}{\sigma_{ys}} \right)^2$<br>(in) | $25 \left( \frac{J_Q}{\sigma_{flow}} \right)$<br>(in) | $50 \left( \frac{J_Q}{\sigma_{flow}} \right)$<br>(in) |
|----------|-------------|-----------|-----------|-----------|--------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|
| Fe-5% Ni | 298         | 1.80      | 1.23      | 1.22      | 1.84                                                   | 16.1                                                        | 0.36                                                  | 0.72                                                  |
|          | 195         | 1.85      | 1.23      | 1.18      | 3.3                                                    | 20.9                                                        | 0.36                                                  | 0.72                                                  |
|          | 111         | 1.92      | 1.23      | 1.12      | 2.4                                                    | 9.1                                                         | 0.20                                                  | 0.40                                                  |
|          | 76          | 1.81      | 1.23      | 1.20      | 1.47                                                   | 1.60                                                        | 0.04                                                  | 0.08                                                  |
|          | 4           | 1.84      | 1.22      | 1.19      | 0.25                                                   | 0.25                                                        | 0.01                                                  | 0.02                                                  |
| Fe-6% Ni | 298         | 1.88      | 1.25      | 1.16      | 3.2                                                    | 20.7                                                        | 0.46                                                  | 0.93                                                  |
|          | 195         | 1.82      | 1.25      | 1.23      | 2.5                                                    | 24.9                                                        | 0.53                                                  | 1.07                                                  |
|          | 111         | 1.86      | 1.25      | 1.17      | 2.6                                                    | 14.1                                                        | 0.40                                                  | 0.81                                                  |
|          | 76          | 1.86      | 1.25      | 1.18      | 2.6                                                    | 6.2                                                         | 0.20                                                  | 0.40                                                  |
| Fe-9% Ni | 298         | 1.83      | 1.22      | 1.21      | 3.3                                                    | 10.8                                                        | 0.27                                                  | 0.54                                                  |
|          | 76          | 1.85      | 1.25      | 1.17      | 2.5                                                    | 3.5                                                         | 0.14                                                  | 0.29                                                  |

\*  $K_{IC}$  value obtained from J-integral results



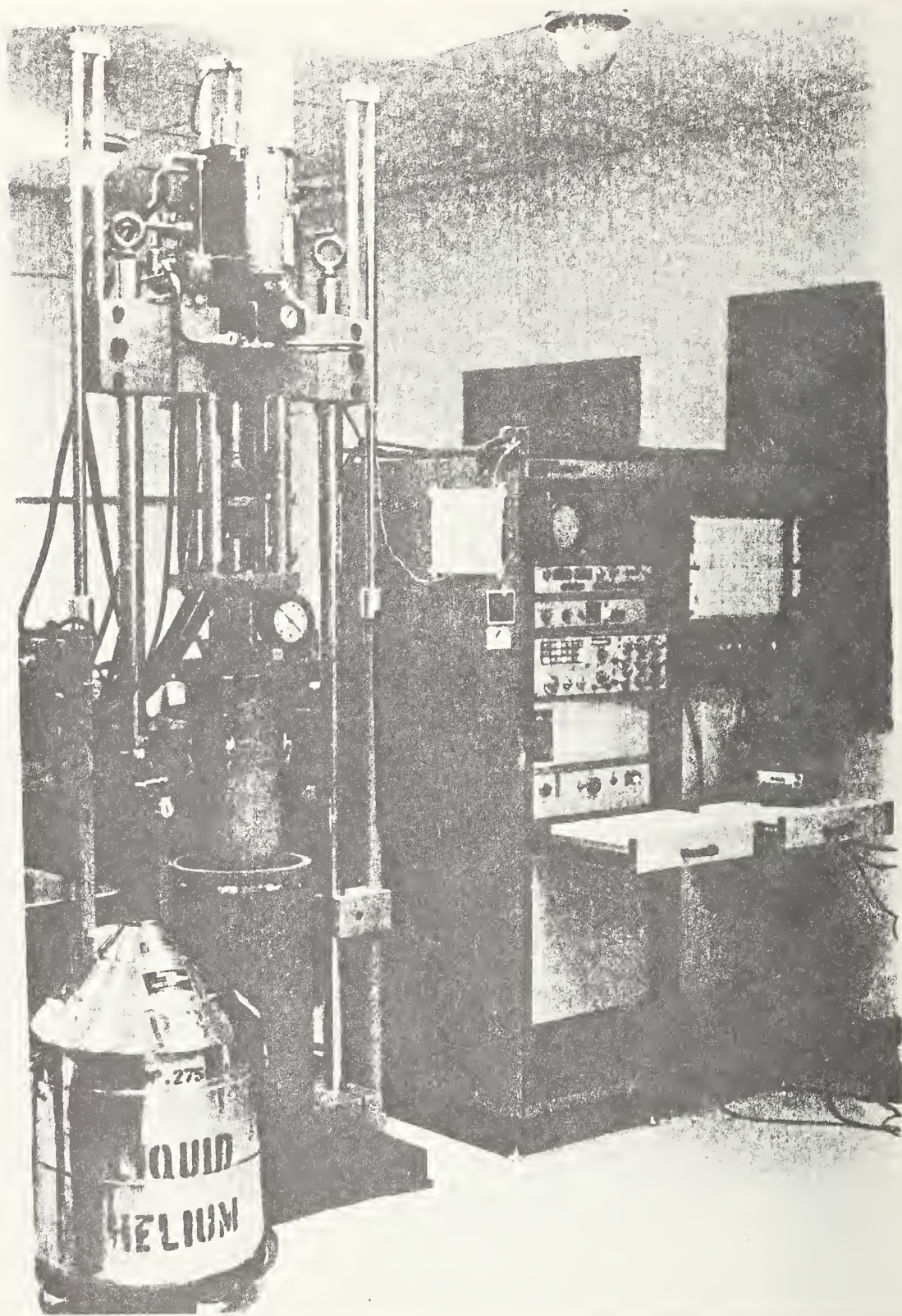


Figure 2 Cryogenic Fatigue Testing Apparatus

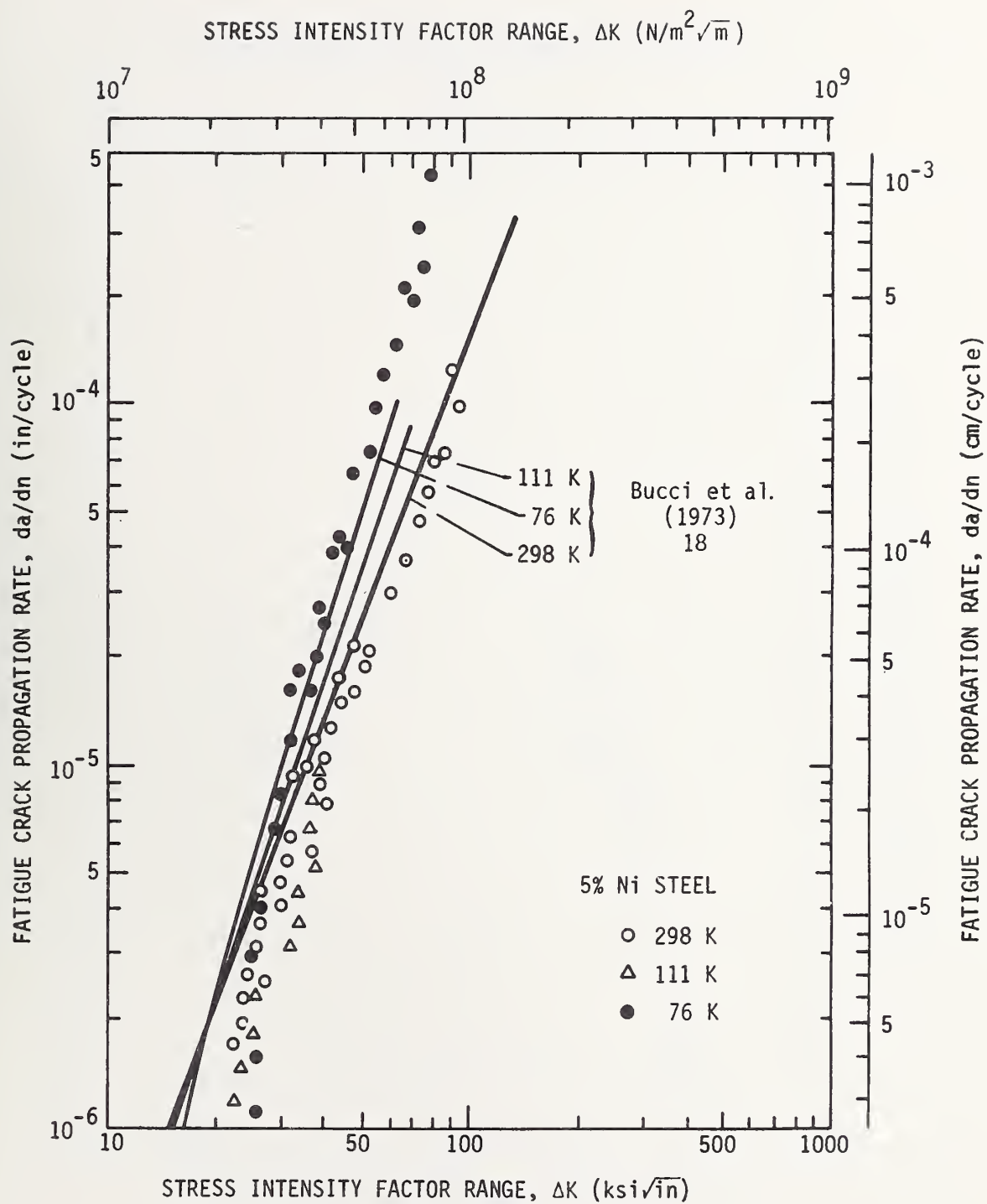


Figure 3. Fatigue Crack Growth Rate of Fe-5 Ni



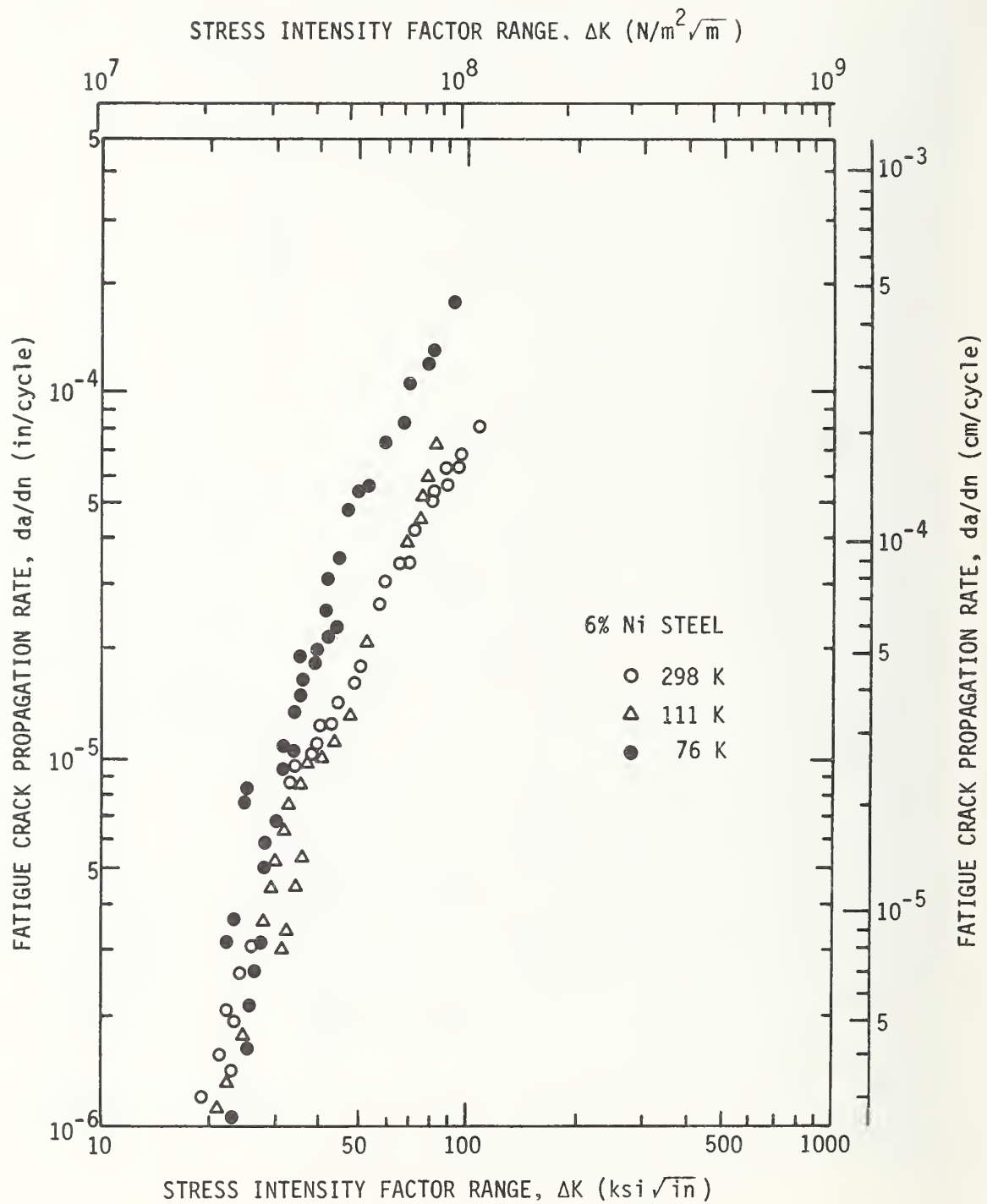


Figure 4. Fatigue Crack Growth Rate of Fe-6 Ni



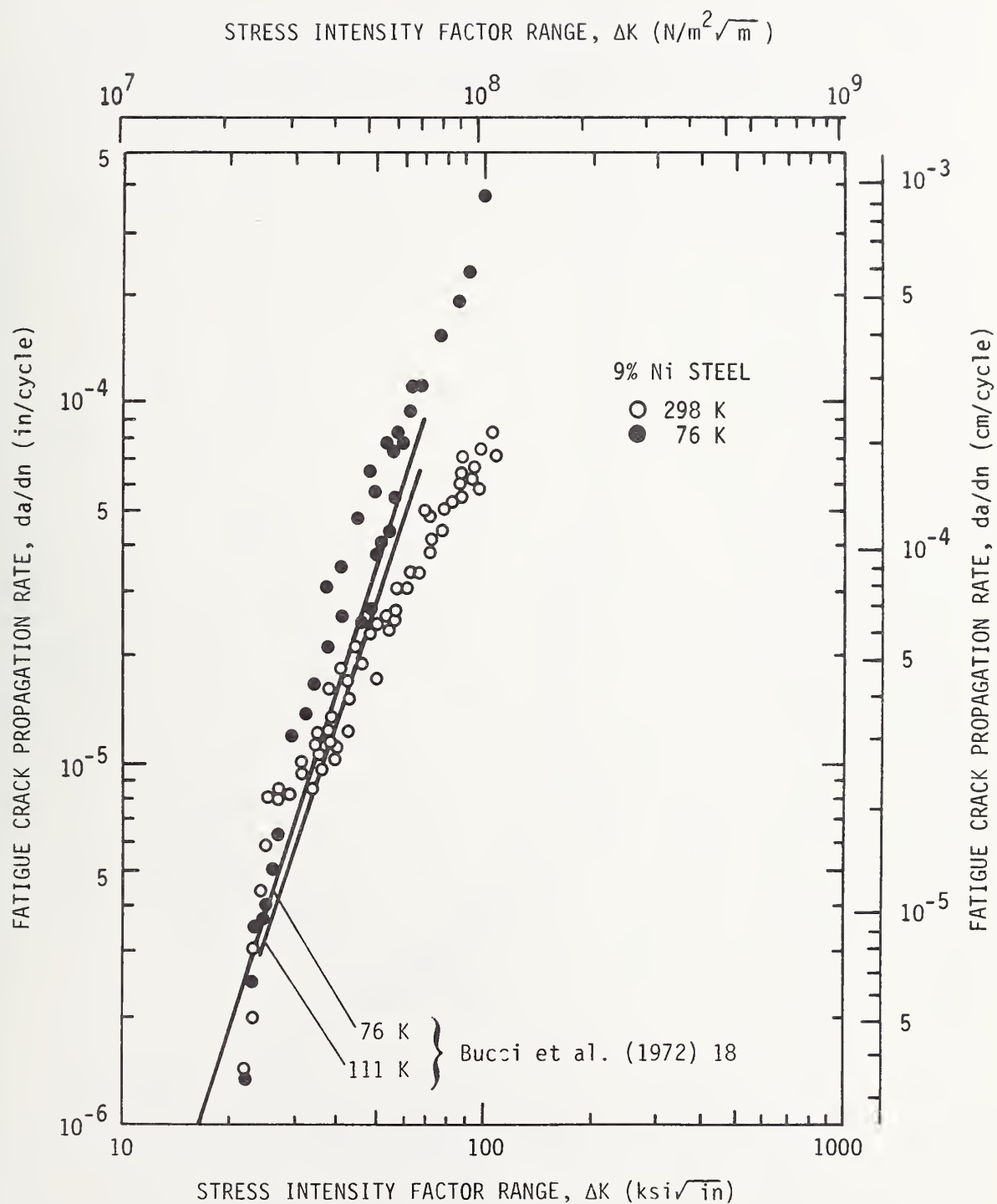


Figure 5. Fatigue Crack Growth Rate of Fe-9 Ni

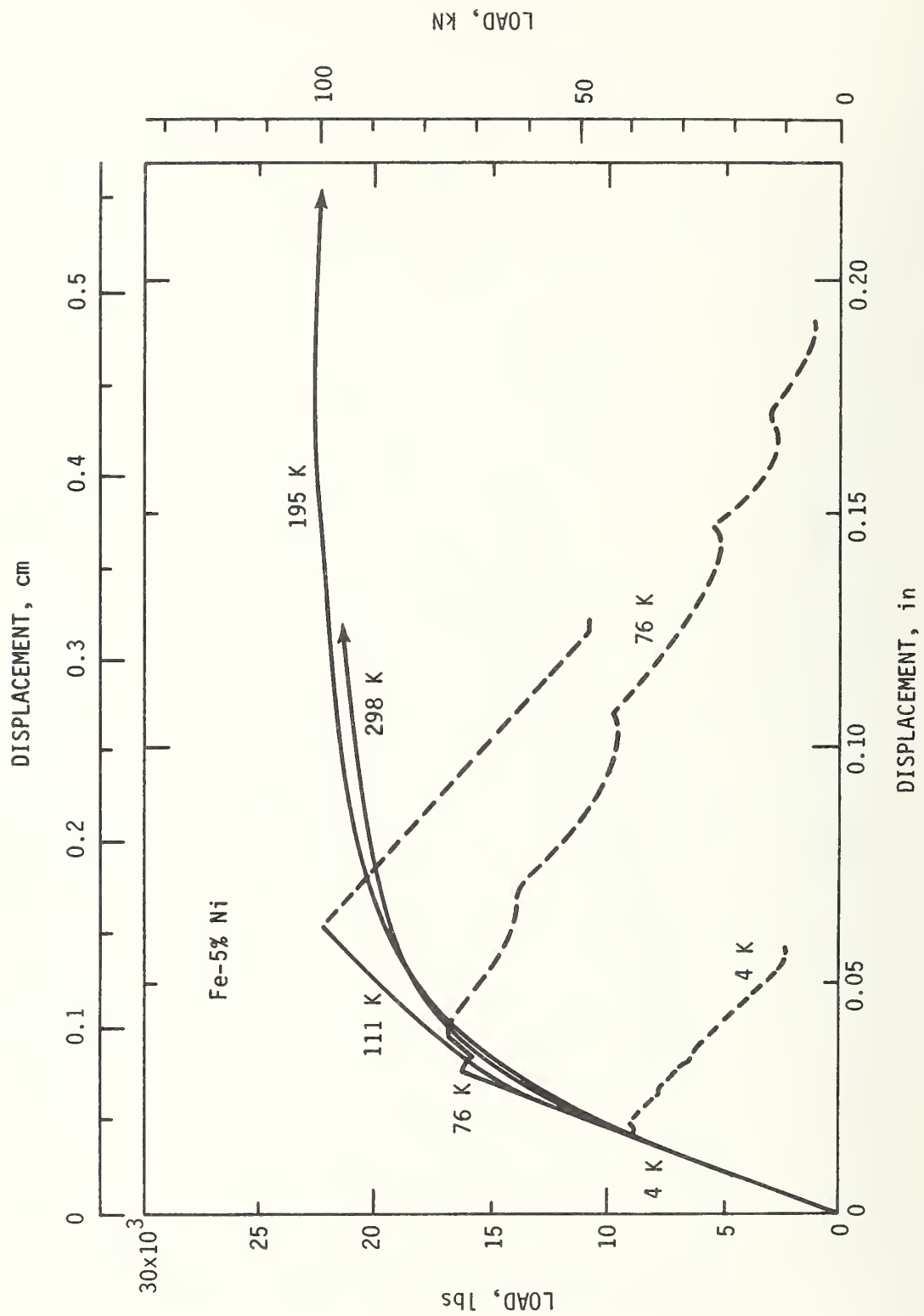


Figure 6. Load-Loadline Displacement Curves for Fe-5 Ni

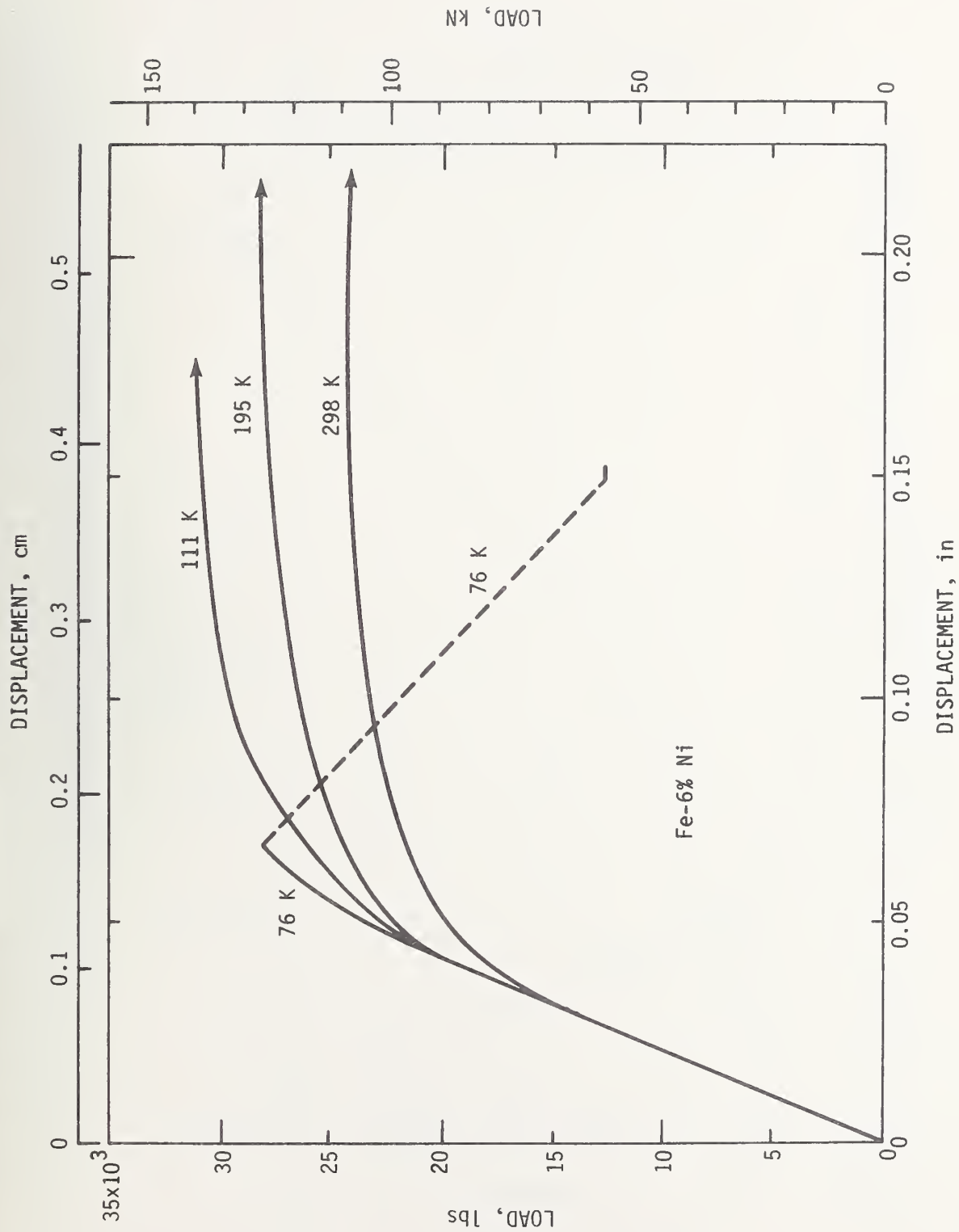


Figure 7. Load-Loadline Displacement Curves for Fe-6 Ni

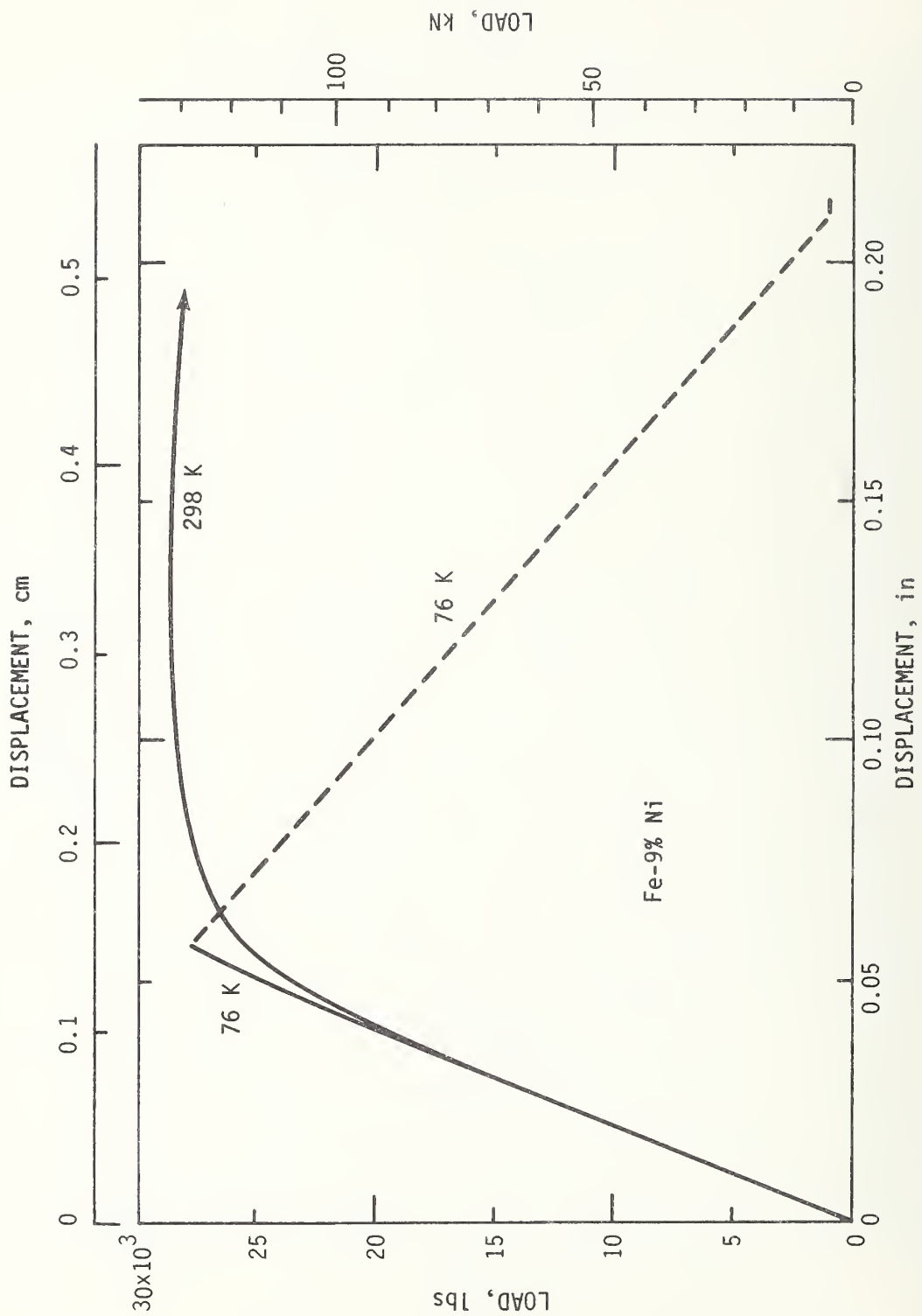


Figure 8. Load-Loadline Displacement Curves for Fe-9% Ni

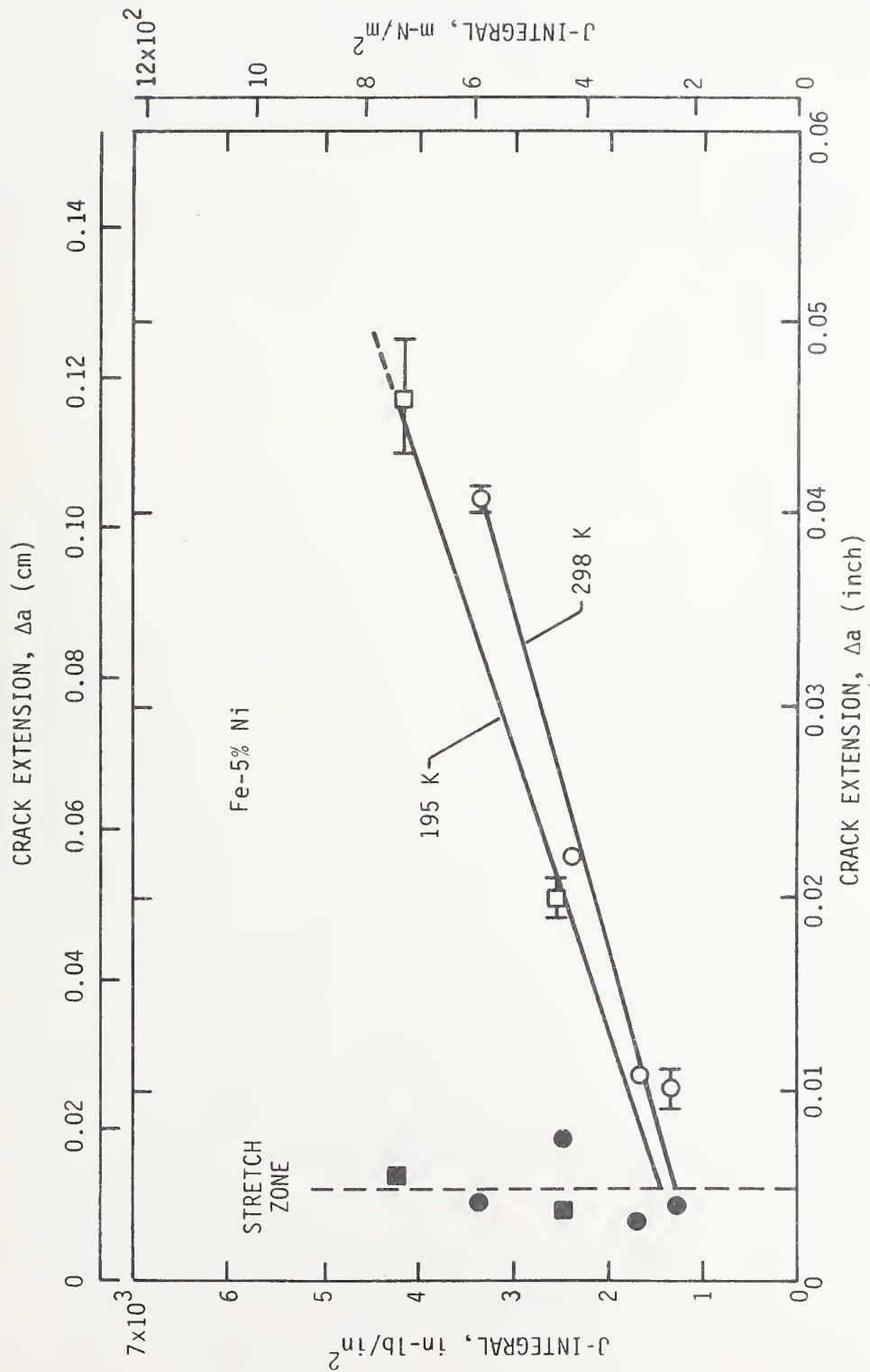


Figure 9. J Resistance Curves for Fe-5 Ni



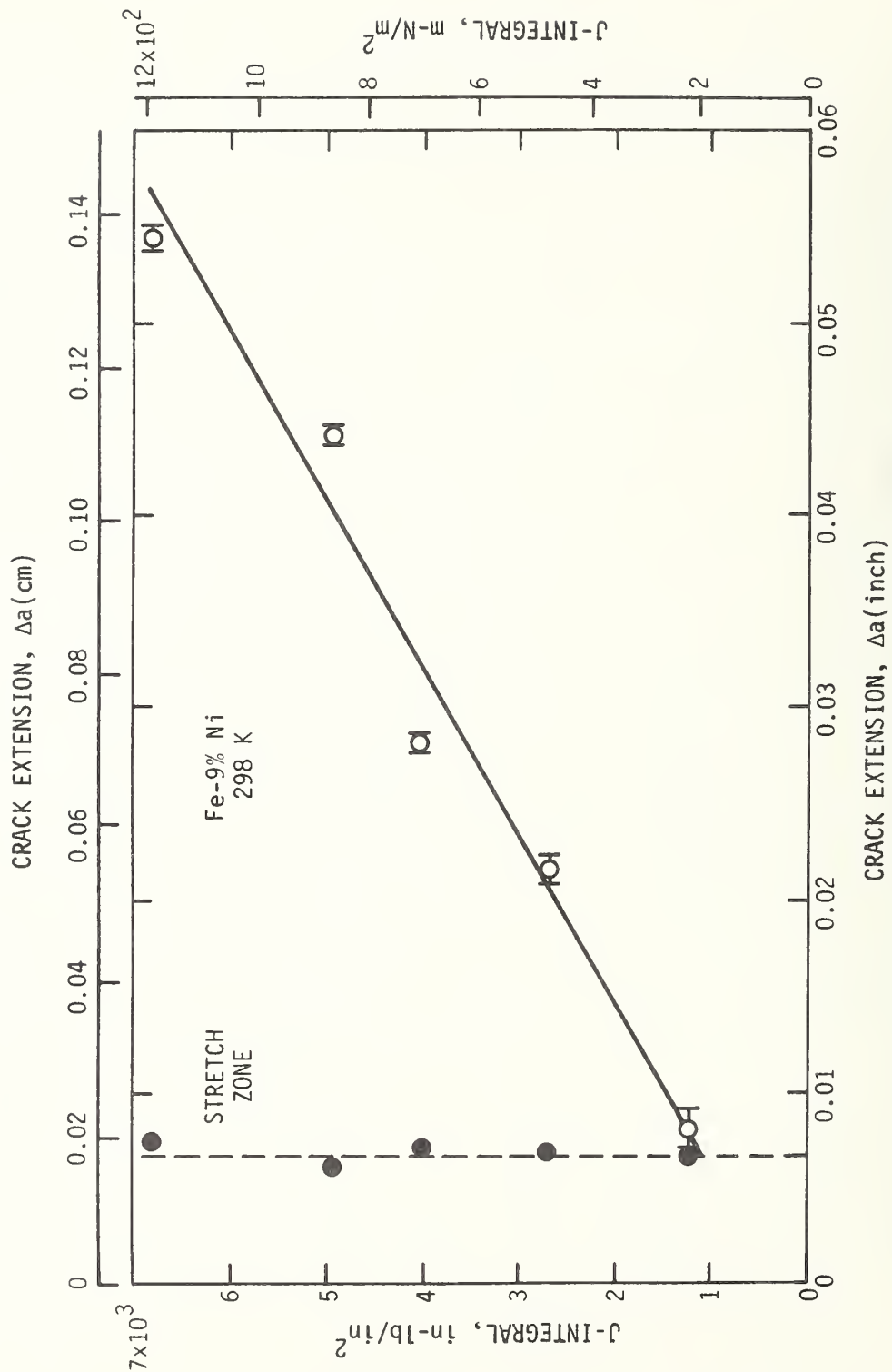


Figure 10. J Resistance Curves for Fe-9 Ni

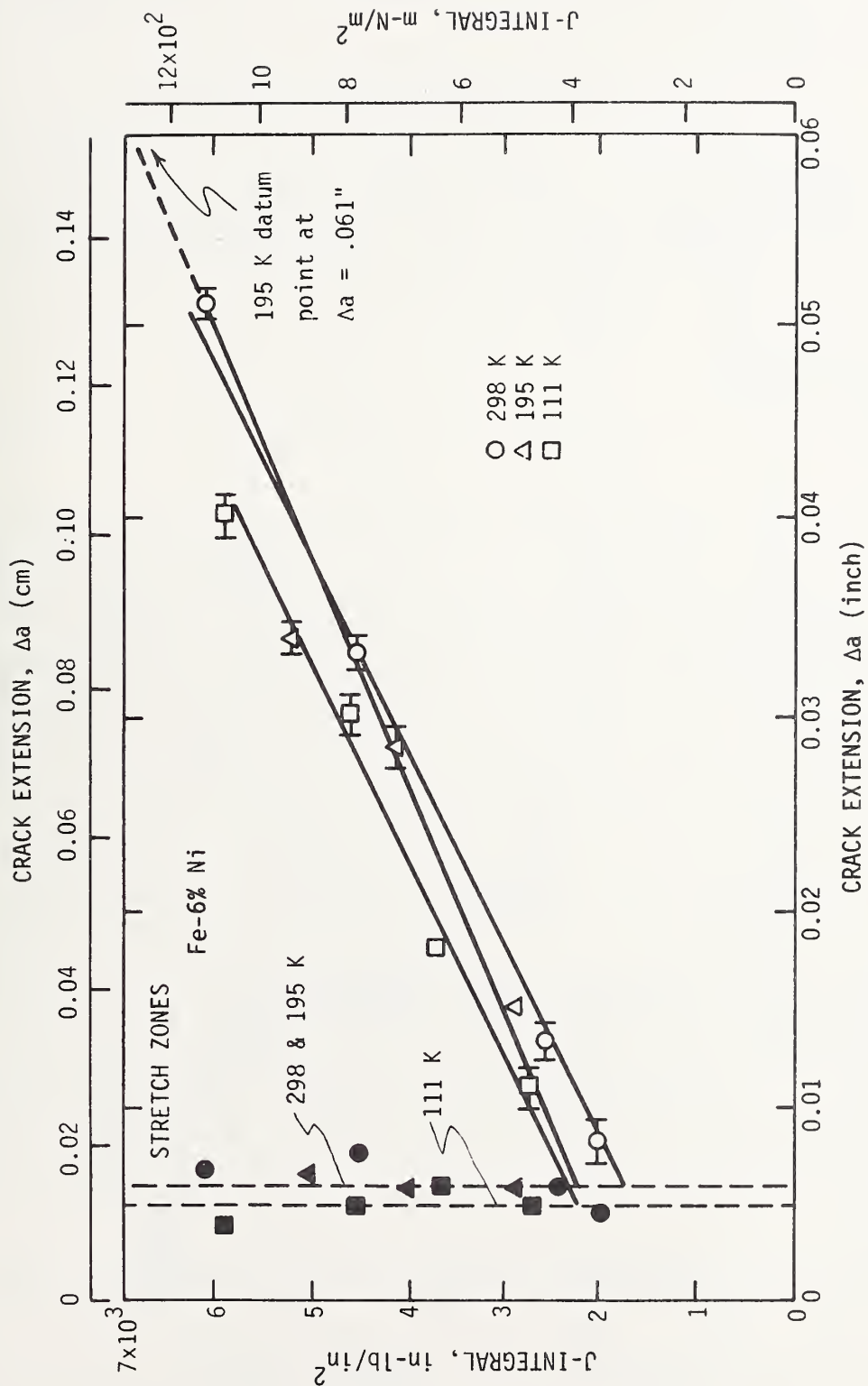


Figure 11. J Resistance Curves for Fe-6 Ni

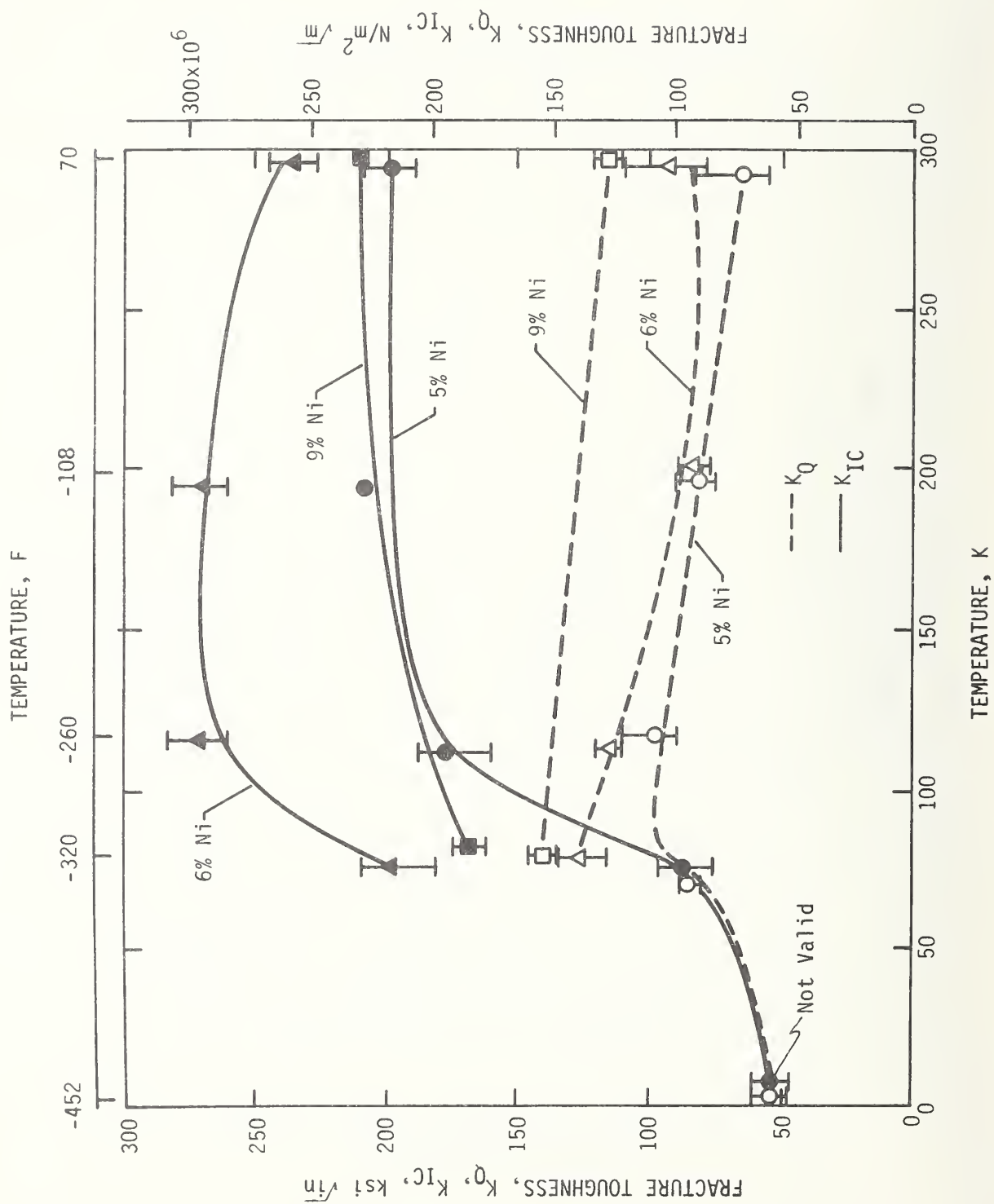


Figure 12. Temperature Dependence of the Fracture Toughness of 5, 6, and 9% Nickel Steels

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                  |                                                            |                              |
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| U.S. DEPT. OF COMM.<br>BIBLIOGRAPHIC DATA<br>SHEET                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1. PUBLICATION OR REPORT NO.<br><br>NBSIR 74-373 | 2. Gov't Accession<br>No.                                  | 3. Recipient's Accession No. |
| 4. TITLE AND SUBTITLE<br><br>Liquefied Natural Gas Research at the National Bureau of Standards                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                  | 5. Publication Date<br><br>Jan 1 - June 30, 1974           |                              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                  | 6. Performing Organization Code                            |                              |
| 7. AUTHOR(S)<br>D. B. Mann (Editor)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                  | 8. Performing Organ. Report No.                            |                              |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br><br>NATIONAL BUREAU OF STANDARDS<br>DEPARTMENT OF COMMERCE<br>WASHINGTON, D.C. 20234                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                  | 10. Project/Task/Work Unit No.<br><br>2750401              |                              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                  | 11. Contract/Grant No.                                     |                              |
| 12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP)<br><br>Same as Item 9.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                  | 13. Type of Report & Period Covered<br><br>Progress Report |                              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                  | 14. Sponsoring Agency Code                                 |                              |
| 15. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                  |                                                            |                              |
| 16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)<br>Seventeen cost centers supported by seven other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at a 20 man-year level with funding expenditures of over \$500,000. This integrated progress report to be issued in January and July is designed to:<br><ol style="list-style-type: none"> <li>1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.</li> <li>2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.</li> <li>3) Provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paper work at the cost center level.</li> </ol> The contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. Distribution of this document is limited and intended primarily for the supporting agencies. <u>Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature.</u> |                                                  |                                                            |                              |
| 17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)<br>Cryogenic; liquefied natural gas; measurement; methane; properties; research.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                  |                                                            |                              |
| 18. AVAILABILITY <input type="checkbox"/> Unlimited<br><br><input checked="" type="checkbox"/> For Official Distribution. Do Not Release to NTIS<br><br><input type="checkbox"/> Order From Sup. of Doc., U.S. Government Printing Office<br>Washington, D.C. 20402, <u>SD Cat. No. C13</u><br><br><input type="checkbox"/> Order From National Technical Information Service (NTIS)<br>Springfield, Virginia 22151                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                  | 19. SECURITY CLASS (THIS REPORT)<br><br>UNCLASSIFIED       | 21. NO. OF PAGES             |
| 20. SECURITY CLASS (THIS PAGE)<br><br>UNCLASSIFIED                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                  | 22. Price                                                  |                              |











